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PHOTOGRAPHIC SILVER HALIDE DIFFUSION PROCESSES

André Rott and Edith Weyde

The evolution of photography
has been marked by a vast number of improvements
but very few real inventions
like Diffusion Transfer Reversal.
Photography had to wait for about 100 years
before this inventive step was taken.
Nowadays, the DTR-process
can no longer be separated from photographic
techniques and is widely applied to materials,
wherever it is essential
rapidly to produce a direct positive.
The idea matured
almost simultaneously and independently
in the minds of André Rott and Edith Weyde.
It was again independently and simultaneously
developed and successfully marketed
by the Gevaert Organisation in Antwerp
and the Agfa Organisation in Leverkusen
in the late 1940's as the first office copying method
which made no use of a dark room
or conventional processing.
The attraction and importance of this book
is twofold.
It offers the first systematic and definitive survey
of the DTR process
about which literature has been extremely scant.
Moreover it has been compiled and edited
by the two original inventors of the process
with contributions from 13 leading scientists
in the research divisions of
the Gevaert-Agfa NV in Belgium
and the Agfa Gevaert-AG in Germany.
In the introduction Rott and Weyde describe
how they independently discovered the new process
and how it grew to full industrial maturity.
In subsequent chapters the structure,
the chemical technology, and the processing
of the copying materials are treated in detail.
Each chapter ends
with a summary of literature and patent references.
A special chapter is devoted
to DTR-office copying equipment as well as
to the economics of the office copying market.
In addition, the different characteristics
and materials based on DTR
in the production of offset printing plates
are discussed.
This field of application is still expanding.
Other printing systems are included which,
though they have not reached production stage,
hold some promise of future development.
There are useful hints for the application
f the DTR-process to aerial and X-ray photography.
The last chapter is devoted to
theoretical fundamentals covering the mechanism
of photographic development, solubility products,
and the complex compounds of silver salts,
as well as the kinetics of the proc-

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Publishers
FOCAL PRESS LIMITED
31 Fitzroy Square, London, W.1, England

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THE FOCAL PRESS

London and New York

ISBN 0 240 50726 6

Text set in 11/12 pt. Monotype Times New Roman, printed by letterpress, and bound in Great Britain at The Pitman Press, Bath

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PREFACE

It is a remarkable fact that since the original invention of silver-halide black-and-white photography by Fox Talbot, there have been very few really fundamental photographic inventions. The evolution of photography has been marked by a vast number of improvements, often very ingenious, each one for instance increasing the sensitivity, both general and spectral, decreasing the granularity, fog and tendency to loss of speed on keeping; but all the time we have been stuck with a negative/positive process and with wet processing.

It is often stated that one of the very real advantages of the negative/positive processes lies in the ability to print any desired number of non-laterally reversed paper positives from one negative. This sort of statement patently misses the point: if a photographic process were to yield a positive directly, one could still prepare any number of non-laterally reversed positives.

The diffusion-transfer process is one of the few genuinely original inventions in photography. In photography we are accustomed to use the word reversal to describe a direct-positive process; hence the term DTR (diffusion transfer reversal) which is used for the processes which are the subject of the present book.

In one-print amateur cinematography, and also in the preparation of colour transparencies, use is made of the fact that in each developed, but unfixed negative, a positive is present in the form of the remaining silver halide. In these conventional processes, after the negative silver image has been removed, uniform exposure and development yield a positive image on the same base, and this positive does not give a laterally reversed image on projection.

In retrospect, it would appear to have been a simple matter to transfer this image to a receiving base, with the additional advantage that the negative silver image remained intact and thus to obtain a non-laterally reversed positive print as well as, at least potentially, a finished negative.

Nevertheless, photography had to wait for about 100 years, before this inventive step was taken, and then the idea matured, almost simultaneously and independently in the minds of no fewer than three inventors to whom the term genius can very fittingly be applied: Rott and Weyde, who are responsible for the present book which is devoted to Document Copying, and Land who will be the author of the second book in this series on Instantaneous Photography.

It does take a genius to see the step which, in retrospect, seems so simple. The reward both to the users and the manufacturers of the invention of the DTR process has been enormous. The rapidity with which a direct practically dry positive print can be obtained is breathtaking; the financial success has been outstanding. It is clear that we have witnessed so far but the beginning of a

new branch of photography which is characterized by its very economical use of that precious material—silver; much more is to come.

Systematic literature on DTR is scant. Hence one welcomes very warmly the arrival of books devoted to this new process. The authors of the present book, now that they have retired from their daily industrial employment have set up for themselves a fitting memorial to their efforts and achievements, which will find a worthy place on the shelves of many a photographic scientist and technologist. In doing so, they have had the benefit of the experience and knowledge of the many contributors named in the contents, whose valuable assistance they gladly acknowledge.

W. F. BERG

INTRODUCTION AND DEFINITION

The processes based on the principle of silver salt diffusion and known by the name of DTR-process* in the technical literature now look back on a past of more than 30 years. Nevertheless, at present they are still regarded as novelties in photographic technique although with various embodiments they have found a wide field of application and consequently have become of considerable industrial importance.

These silver salt diffusion processes are characterized by the simple and rapid production of positive images. This is facilitated by the use of appropriate mechanical aids, so that silver salt diffusion processes have rapidly been adopted in this age of speed and technical progress. Just as in other photographic processes, a silver halide emulsion layer is first used for recording the negative image. The unexposed silver halide is used for composing the positive image, as in the well-known older reversal processes such as those using reversal film, Photomaton-images, etc. The latter processes, however, require rather cumbersome processes in several baths.

In the silver salt DTR-process, however, the positive image is formed almost simultaneously with the negative image by treatment in the same bath. This progress has been made possible by the use of very simple expedients, such as the addition of a silver halide solvent to the developer and the use of a second layer, which is in intimate contact with the negative layer during the development. This second layer contains development nuclei which are produced chemically and are capable of reducing the diffusing, unexposed silver salts. The physical and chemical processes taking place occur simultaneously or consecutively within a very short space of time and this is characteristic of all silver salt diffusion processes and is the reason for their great success.

The existing silver salt diffusion processes differ from one another not only in their applications but also as regards the sensitivity of the negative, the composition of the positive layer, the nature of the developer, the kind of processing, etc.

It thus seems appropriate to discuss separately the main fields of application of the silver salt DTR document copying process, which above all is related to duplication processes and image-recording processes and to which instant photography by the Land Polaroid process and materials for aerial and space photography as well as for radiography belong. In the present book, the main problems dealt with are those which are connected with document-copying.

* The expression "Inversion-transfert par diffusion" was proposed by Professor L. P. Clerc, editor of *Science et Industries Photographiques*, when he published for the first time a study on the new process (Sc. et Ind. Phot., July 1942). The expression "Diffusion-Transfer-Reversal" which is in fairly current use in English technical literature, was first employed by Professor L. E. Varden (C. B. Neblette, *Photography, its materials and processes*, Fifth Edition, 1952).

The work of Land and his collaborators is discussed mainly when it is also of interest in document-copying.

In the scientific and technical literature there are relatively few references to the silver salt diffusion process. Some of them are distributed over a wide range of subjects. On the other hand, the patent literature is very rich in such references, but the study of these patents is rather difficult because of the abundance of partially overlapping statements. Consequently, it seemed to be appropriate to summarize the various references and publications.

Rapid progress has been made in introducing new principles into the technique of photography, e.g. physical methods such as electrophotography, magnetic processes, etc., which in many cases can replace the conventional method of silver salt photography. Yet many routine workers in the art believe that the silver salt diffusion processes will still survive for a long time because of their specific properties as described on this monograph.

If this monograph is able to smooth the way for new investigations and further progress in this field, it will to a great extent have achieved its object.

I. HISTORY OF THE DTR PROCESS

1.1 *Introduction*

If the Goddess of Fortune is alleged to be capricious, the invention of the DTR process provides a case in point. The principles of the process were discovered independently and at nearly the same time in the laboratories of two industrial organizations, Gevaert Photo-Producten NV of Mortsel and Agfa AG of Leverkusen. Apart from one or two abortive attempts, no product based on this discovery was marketed during the next ten years. Eventually when DTR office-copying had become a commercial success surpassing the most optimistic expectations, the two firms engaged in very sharp competition.

Today these two companies have merged to form a single concern (Agfa-Gevaert). The respective inventors, now both retired, relate the circumstances which led them to their discovery of the DTR-process.

1.2 *Process of André Rott, Gevaert Photo-Producten NV, Mortsel (Belgium)*

The phenomenon of DTR was discovered in our laboratories quite by chance—it was nevertheless the result of an investigation which had a definite goal, and which had been carried on over a relatively long period.

In 1935 Mr. Lieven Gevaert, the brilliant founder of the firm, issued an order to the effect that incoming letters should no longer be sent to the various departments in the factory, but should be distributed in the form of photographic copies. At first this measure was received with scepticism—loss of time, waste of materials, etc. After a short time however, it proved to be very useful and once it had been generally adopted it soon became indispensable. Letters no longer got lost, problems could be studied simultaneously by different people—each department could organize its own files and documentation. Today we know the immeasurably important role played by office copying in almost every branch of information.

Before the introduction of the DTR-system, a reflex method was used for office-copying: a light-sensitive, so-called document paper was placed in close contact with an original and exposed through its back surface. After developing and fixing a negative was obtained. It was impossible to read this negative (as it was laterally reversed), and it therefore had to be copied again on to a second sheet of document paper, so that the entire process had to be repeated (exposure, development, fixing, washing, drying), in order to obtain a readable copy.

To simplify this process and thereby save much labour was an attractive aim, and I did much research to this end. The idea was as follows: if, after development, the negative layer could be separated from its base and then transferred to another paper surface, a negative but readable copy—white letters on black background—would be obtained. It was clear that this system would result in the economy of time, work and photographic material.

Although the idea was good, it was not easy to put into practice. The negative emulsion layer which was to be stripped off was coated on to a specially prepared paper support bearing a hydrophilic stripping layer. After reflex exposure it was immersed for a short time in a developer and by means of a rubber roller was then squeegeed on to a specially coated paper, which was to serve as the base of the copy. The paper base of the negative material could of course easily be stripped off after the squeegeeing process and a well-developed image became visible. However, difficulties arose during the subsequent fixing process: the transferred emulsion layer showed a tendency to come away from the paper, especially at the edges, and the resulting copy was often faulty and unsuitable for use.

Discouraged by these unsuccessful attempts we almost gave up the idea until one day early in 1938 unexpectedly brought us new hope: under (a portion of) the negative layer, which had become unstuck during the fixing process, a faint but clear positive image appeared (Plate 1.1).

Suddenly a solution became evident: why make vain efforts to transfer the negative layer, when a positive image could be obtained immediately?

Then began a period of intense activity: to reproduce the phenomenon, which had been accidentally observed—to disclose the causal connections—to make the phenomenon reproducible—to intensify the faint image—to convert the originally brown image into a black one, etc. It was obvious from the beginning, that the image was composed of silver and that it had been formed at the expense of the unexposed silver salts, which were transferred, by diffusion, to the new surface: the process of silver salt diffusion, the DTR process, was born!

Much later, when the new system had become a promising reality, someone remembered that the phenomenon of image-transfer had already been observed several years earlier but had not been recognized at the time. A photographic customer of Gevaert Photo-Producten NV, reported that, when enlarging transparencies on reversal paper a slightly underexposed copy had been thrown away. After turning on the white light he found developed negative adhering to the back of another paper in the refuse bin. On separating the two papers he found—to his surprise—a plain positive image on the back of the second paper. The image was sent to the firm; however, no explanation could be found and interest in the case eventually waned. The hour of the DTR-process had not yet come.

A patent for the new system was filed (BP 614,155) in November 1939, and

shortly afterwards the first DTR-office copying paper was marketed under the name "Transargo". Later another DTR-material, "Diaversalpaper" was introduced. This material enabled positive enlargements to be made economically from transparencies. Both these processes are described later in this book.

1.3 *The Process of Edith Weyde, Agfa AG, Leverkusen (Germany)*

The discovery of the fundamental principles which had to be made before DTR-systems could be put into practice was due to a number of coincidences which occurred in the short period during which attempts were being made to resolve a number of problems, which, in some way or other, were connected with the DTR-system.

When dealing with customers' complaints it often appeared that many of the faults arose from the use of a developer which was more or less contaminated with sodium thiosulphate. This resulted in the formation of yellow fog, mainly at the edges of the prints, or of stains. By chance, it was found that this yellow fog was not formed in the emulsion layer, but in the baryta layer. If the emulsion layer was stripped from the base, a weak but nevertheless sharp negative copy of the positive image was found to be left behind in the baryta layer. At first sight it would appear that the image had been formed by the solution of a very small quantity of the silver halide in the sodium thiosulphate with which the developer was contaminated. These salts had diffused into the baryta layer and were then reduced to silver by some unknown phenomenon.

Sometimes we obtained images which exhibited an unsharp negative image on the back of the paper. Faults of this kind could be reproduced by fixing in solutions which had already become alkaline, or by fixing a large number of sheets of photographic paper without agitation. In this case, the silver salts diffused on to the back surfaces of the other materials where they were reduced to silver in the paper fibres.

In the first instance it was clear that the following conclusions could be drawn: the unexposed silver halide in a layer is capable of being dissolved and reduced to silver in a second layer. Whenever there was close contact between the two materials the resulting images were always sharp.

Another fault emanated from a very strange kind of colour fog which was noticed during the processing of Agfacolor films. In this material—the research was carried out in 1937–38—a yellow filter layer of colloidal silver was coated between the upper layer (containing a non-diffusible compound for the formation of the yellow dye) and the central one (containing a non-diffusible compound for the magenta dye).

The colour fog was always found at the lateral edges of the upper and central layers which were in contact with the yellow filter layer. A large number of tests proved that the fog was formed as follows:

Small quantities of silver halide are first dissolved in the colour developer (a substituted derivative of p-phenylene-diamine) and then diffuse towards the filter layer where they are reduced to silver. The presence of colloidal silver in this layer greatly accelerates the reaction.

The oxidation products of the colour developer diffuse into the neighbouring layers, encounter the non-diffusible compounds and react with them to form the respective yellow or magenta dye. If small quantities of sodium thiosulphate are added to the developer, the colour fog is intensified: if no colloidal silver is present then no colour fog can be seen. Two conclusions could be arrived at from these observations: In order to promote the migration of silver salts from one layer into another, their reduction must take place rapidly. This occurs when nuclei—in this case colloidal silver—are present.

During the same period, much time and labour was expended on the study of stabilizers, and the experiments which were carried out in this field complemented the hypotheses which are described above.

In layers which did not contain any stabilizer, a yellow fog was formed when developers contaminated with sodium-thiosulphate were used. The colour of this fog ranged from dark blue to violet when the layers contained 1-phenyl-1H-tetrazole-5-thiol. A first indication of the mechanism underlying the change in the colour tone of developed silver from yellow to black was obtained in this way. As long ago as 1939, Agfa AG brought out a photographic paper called "Copex Autorapid" which contained the developing agents in the layer thus permitting the material to be rapidly processed. The experience obtained in evolving this paper proved very useful in the further elaboration of DTR-materials (see G. Schaum and E. Weyde: Agfa Veröffentlichungen VI, p. 198 (1939)).

The experience gained led to consideration being given to the design of a material which would give a direct positive by utilizing the DTR-principle. This goal was very soon reached. The very first applications of these materials were found to be in a kind of instant photography and not in photocopying sector. It was not until 1940 that the first copies based on the same principles were made.

During World War II the new materials were used for a large number of other purposes, such as the rapid processing of aerial photographs. After the war, a situation had developed in which Agfa AG was obliged to carry out its research in a single field: the choice fell on office copying materials, as this branch of photography held out the greatest promise of success. Moreover, research in this field had already reached a very advanced stage.

As long ago as 1940 it became evident that the DTR method of office copying could only achieve real success if adequate apparatus were made available. Therefore a device which enabled the materials to be processed mechanically was built in 1940 and a patent was applied for (DT 973,796).

After the war the introduction of DTR materials was held up in the first

instance by the need to elaborate the processing equipment required for office purposes and thus the DTR method of copying with "Copyrapid" materials did not make its appearance until October 1949.

The first product to be based on DTR-principles, was brought out by Agfa AG under the name of Veriflex. This was a transparent paper which gave direct-positives and which was intended to serve as the original for making copies by the diazo method.

This paper was provided with a zinc oxide layer containing silver nuclei on top of which an unhardened silver chloride layer was coated. The zinc oxide was necessary in order to enable a reflex exposure to be made. After exposure and development the upper layer showing a negative of the original was washed-off with warm water, whilst the zinc oxide was dissolved out by means of acetic acid. This paper was available during the war. Later it was replaced by the Copyrapid materials which provided a much easier method of making positives on a transparent base.

The DTR-system has met with rapid success in spite of its rather doubtful prospects. It has required much further research and development, of which a comprehensive survey is given in the following chapters.

We are indebted to Dr. A. Leubner, formerly director of the department of the manufacture of the photographic papers of Agfa AG, Leverkusen, for many stimulating ideas, particularly in regard to processing apparatus.

The further development of the DTR-process has been made possible by the work of many of my colleagues.

1.4 *The predecessors of the DTR process*

Neither Rott, nor Weyde had any reliable sources of documentary information to which they could refer when working on the DTR process. They discovered independently the principles of the system during their experimental work, and both found a means of working out a practical system on the basis of this knowledge.

Nevertheless a certain number of publications were known which dealt with or at least mentioned some of the problems which were related to DTR. The transfer of silver salts from one layer to another, the accelerating action of nuclei on the reduction of the silver salt during physical development and the possible use of diffusion phenomena to form an image were basic principles which were already known.

As long ago as 1857, B. Lefèvre discovered the phenomenon of silver transfer when processing Daguerreotype-plates. When a sheet of paper covered with a gelatin layer was pressed into contact with a moist Daguerreotype plate which had just been developed and had been soaked in thiosulphate, he found that after a few minutes, an image on the gelatin layer had been formed by the

reduced silver in the plate. In order to intensify this weak negative metallic image, he proposed using the transferred silver grains as catalytic centres, on to which reduced silver could be deposited.

Stevens and Norrish made analogous observations in 1938 when studying various photographic reversal phenomena. They pressed a so-called process-plate (slightly developed and soaked with developer) into close contact with a plate covered with a gelatin layer which had also been moistened with developer solution. When the light-sensitive plate and the gelatin plate were separated from each other a positive image was formed in the gelatin layer in a couple of minutes after the latter had been further developed in an acid physical developer. The investigators explained the phenomenon as follows: the unexposed, but slightly fogged silver salt resulting from the first development had diffused into the gelatin layer to form nuclei for the further process of physical development. This hypothesis was supported by the fact that the latent image in the gelatin layer could not be washed out with water and was only slightly reduced when the material was treated with thiosulphate.

Moreover a microscope study of the layers revealed that the transferred silver was dispersed throughout the entire thickness of the layer and not only over the surface of the layer.

H. Ahrens and J. Eggert had reported earlier in their publications on the growth of colloidal silver in gelatin layers that the presence of silver nuclei accelerated the reduction of silver salts during physical development. An experiment which was designed to deal with a subsidiary problem which arose in the DTR-process, was described in 1898 by R. E. Liesegang. When a fairly heavily exposed silver-chloride gelatin emulsion (Aristo-emulsion) was placed in contact with a gallic acid developer in the form of a gel and stripped off after development, a negative print of the original was obtained in the gel layer. R. E. Liesegang explained this as follows: the silver nitrate which is present in the light-sensitive layer diffuses from the unexposed areas into the gel layer where it is reduced by the gallic acid.

Apart from these investigations the use of diffusion phenomena for obtaining images has also been described in the literature. These phenomena are, however, only partly involved in the DTR-process.

The investigations of E. Stenger and A. Herz, who in 1923–24 discovered a mechanism for obtaining positive images by means of the image-wise diffusion of developer substances are worth mentioning. An exposed silver bromide layer was moistened with a developer solution and placed in contact with a second, uniformly exposed layer. An image was formed on the latter by the transferred unused developer. Further examples of the use of diffusion phenomena for obtaining images are the Carbro and the Ozobrom systems in which an existing silver image is converted into silver halide and transferred by diffusion on to a layer in contact with it; the resulting image is formed by tanning phenomena.

This survey of the work of these predecessors may prompt one to ask why the DTR-process was discovered at so late a date, relatively speaking, in the history of photography. This question may possibly be answered by saying that good, usable results are only obtainable when all the parameters in a reaction lie within certain concentration limits. The finding of these tolerances was no simple matter, and a chance discovery on the one hand and systematic investigation on the other hand were necessary to pave the way to making this remarkable evolution in photography a practical reality.*

* Chapter 28 of Neblette's "Photography, its Materials and Processes" is largely devoted to a description of the predecessors of the DTR-system. This chapter also contains a list of publications which appeared just after the war when the DTR-process became known. These publications which deal essentially with the interdependence of the materials and the processes, and also some earlier publications, have ceased to be of importance and have therefore not been reviewed here.

II. THE DTR PROCESS

2.1 *The variants and single processes*

The principle of the DTR-process, the advantage of which lies in the quick and direct production of positives, has already been described briefly in the Introduction. The following processes take place successively or simultaneously during the production of a positive print. A silver-halide layer is exposed and developed in the usual way. By the action of sodium thiosulphate which is added to the developer in accurately measured quantities the unexposed silver halide salts become partially dissolved during the development. Thus, a developer solution which contains a certain amount of soluble silver complex salts is formed. This solution is not stable and tends to reduce the silver complex salts to silver. The reduction process can be accelerated by providing development nuclei, consisting, e.g. of colloidal silver. These nuclei are preferably incorporated in the layer in which the positive image is to be formed.

In practice the above-described processes take place as follows.

The light-sensitive silver-halide layer (the negative) and the nuclei layer (the positive) are soaked with a developer containing a small amount of sodium thiosulphate. Subsequently, both layers are brought into close contact by means of, e.g. a rubber roller. The dissolved silver salts in the negative layer diffuse into the nuclei layer where they are very rapidly reduced to silver. In the exposed areas of the negative all the available silver halide is developed to silver. Consequently, no soluble silver compounds can be formed here, which means that the corresponding areas in the positive layer remain clear. Only in the unexposed areas of the negative are soluble silver salts formed, and these salts after having diffused into the nuclei layer, are reduced to silver, thus creating a visible positive image. When the two layers are separated from each other shortly afterwards, the negative image can be seen in the silver halide layer (negative) whereas the nuclei layer shows a positive image of the original. In this embodiment of the DTR-process, the silver-halide solvent can be added either to the developer or to the positive layer. The following figure illustrates diagrammatically the formation of the positive image.

The process can also be carried out with the negative and the positive layers coated on to the same base. For instance, a greatly hardened positive layer, which is not sensitive to hot water, can be coated with an unhardened negative layer. The resulting layer can be exposed and treated with a developer containing sodium thiosulphate. The processes are the same as those which take place in two-sheet materials. The positive is rendered visible by removing the unhardened negative layer with hot water.

When using this layer composition, the silver-halide solvent must be added to the developer, because, for reasons of stability, the developing agent cannot be added to the light-sensitive emulsion.

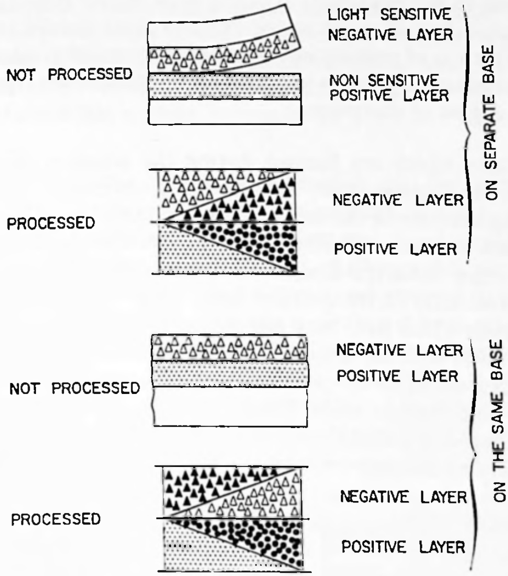

Fig. 2.1. Variants of the DTR process.

A novel variant of the DTR process has been proposed, according to which a negative layer is first coated on to a support, and is then covered with a layer containing nuclei.

If a binding agent, which does not adhere very well to the gelatin of the negative layer, is selected for the nuclei layer, the positive layer can be transferred to another support after processing.

The various possible applications of the DTR process have led to further modifications in processing, and these will be dealt with in more detail in the following section 2.2.

The theoretical principles of the process are dealt with fully in Chapter 6. Only a few partial processes will be described here. This description is necessary for a better comprehension of the following chapters.

When manufacturing DTR materials, two conditions must be fulfilled in order to obtain useful results:

(*a*) The exposed areas of the negative should be developed fully before the unexposed silver halide is dissolved; only in this way can clear highlights be obtained in the positive.
(*b*) the precipitation of silver in the positive layer should proceed rapidly. This condition is of primary importance for the rapid production of images and for obtaining a positive in which all the details are reproduced with a sufficient degree of sharpness.

The silver salts which are formed during the solution of the unexposed silver halide in the negative layer, diffuse in all directions.

However, any decrease in the concentration of the silver salt in certain areas, e.g. by reduction to silver, will result in an acceleration in its rate of diffusion towards these areas. Since it is desirable to transfer the largest possible amounts of dissolved silver salts to the positive layer, care should be taken to ensure that the silver salts which have been transferred to this layer should be reduced to silver in the latter with the utmost possible speed. In practice, this is accomplished by adding nuclei to the positive layer. The nature and action of these nuclei will be described in more detail in chapters 3.2.2, 3.2.3 and 6. To make sure of obtaining a sharp positive image the reduction of the silver salts should, as already mentioned, proceed rapidly, whereas the process of solution can be allowed to take place slowly.

Image formation is greatly influenced by the concentration of the reacting substances. The various factors which influence the absorption of developer solution by the layers, e.g. the nature of the binding agents, the degree of hardening and the addition of salts will all play a part in this image formation. Since uniformity of these factors is essential for the success of this process in practice, the use of mechanical processing aids is generally indispensible.

The nature and concentration of the silver-halide solvent must exert a particularly great influence, because they determine the nature of the complex silver salts. This problem is discussed more thoroughly in chapter 6.

2.2 *Applications of the DTR system*

During the evolution of the DTR system, many applications and variants were worked out. In the following paragraphs a short survey of these systems is given:

2.2.1 SYSTEMS WITH SEPARATE NEGATIVE AND POSITIVE SHEETS. Most of the DTR materials on the market belong to this group.

2.2.1.1 *Office Copying Materials.* These materials may be called the "classical" DTR-materials. They are manufactured by a large number of photographic firms and have attained a very high degree of quality and reliability during the last twenty years. The DTR-materials designed for office copying consists of a negative material of "high" or "low" sensitivity and a wide range of positive materials which have a practically unlimited field of application. The negative and positive are placed in a developer solution, pressed into close contact with each other and, after a short time, pulled apart. The system produces a positive copy which is ready for immediate use. (A more extensive survey of these materials is given in chapter 3.)

2.2.1.2 *Offset Materials.* A. Offset Materials on Paper Base. When a very large number of copies is required, recourse can be had to a system which is derived from the conventional DTR system and which enables about 1,000 copies to be made from a single original. Lithographic properties can be imparted to the resulting positive silver image by subjecting it to a supplementary treatment with a special preparation which renders it hydrophobic, whilst the white areas become hydrophilic. This property can be utilized to form the basis of a simple offset system. Other variants consist either in surrounding the diffusing silver directly with substances that render it hydrophobic or by reducing the diffusing silver complexes with a tanning developer. In both cases a direct hydrophobic image is obtained, so that printing can be done without any further treatment (see chapter 4).

B. Offset Materials on an Aluminium Plate. When a larger number of copies is required, use can be made of DTR-offset materials on an aluminium support instead of on a paper base. The deposition of silver on aluminium can be carried out by means of the following two processes:

In the first method the aluminium plate is provided with a layer of nuclei in which the reduction of the silver takes place. The resulting silver image is then rendered hydrophobic by an after-treatment. The aluminium plate has thus been converted into a support with lithographic properties.

In the second method the aluminium plate is not provided with a layer of nuclei. Since however, aluminium is strongly electronegative and silver is electropositive, the diffusing silver can be reduced electrochemically at the aluminium surface when other heavy metal salts are present. The silver is then rendered hydrophobic by the use of suitable substances.

When an aluminium plate is used as a positive, up to 10,000 and more prints can be made (for details see chapter 4).

2.2.1.3 *Stencil Printing Systems.* During the elaboration of DTR systems, many experiments were performed with the object of manufacturing stencil printing matrices.

In order to arrive at a material of the required properties, the following procedure can be adopted: Yoshino-paper, which is commonly used for stencil purposes, can be provided with a supplementary layer containing developing nuclei. The conventional DTR method can be used to obtain a positive, but openings must be made in the covering layer of the paper to allow for the passage of ink, and this is done by treating the material with hydrogen peroxide, or—when the covering layer consists of wax—by exposing it to infra-red radiation, or again by means of a tanning development during transfer. In the last case an autopositive emulsion has to be used as the negative. The untanned parts of the layer are then washed away after transfer (for details see chapter 5).

2.2.1.4 *Materials for aerial photography and space technology.* Apart from their use in copying and duplicating, DTR systems have also found a large field of application in aerial photography. The great advantage of these materials lies in their ability to furnish a complete, finished set of photographs immediately the aircraft lands. Two systems have established themselves: the Bimat-process and the Ditrecon-system.

In the Bimat process, the negative and positive which were soaked in a developer solution before the aeroplane took off, are brought into intimate contact with one another. Thus slight development of the negative and the transfer of silver to the positive take place during the return flight and when, on landing, the two materials are separated, a positive is already available for interpretation (see chapter 5).

In the Ditrecon-system, the exposed negative and positive material are placed together in an apparatus, moistened with developer and brought into contact with each other. Here again, after separation, a positive which is ready for interpretation is obtained.[1]

2.2.1.5 *Instantaneous photography.* A further application of the DTR techniques has been their use in ultra-rapid photography. A report on this special application is given by E. H. Land, *et al.* in a separate volume. The particular feature of this system lies in the fact that the developing and transfer are carried out in the camera by means of a developer paste. This process takes place so rapidly that a finished photograph is obtained only 10 seconds after the exposure.

Another means of obtaining a positive in a very short time, consists of processing a normal negative film and a positive material together in a developing apparatus analogous to that of the Ditrecon-system. In order to stabilize the negative for further printing by a conventional method it can be fixed in a photographic fixing bath. The advantage of this system is that no special camera is required.[2]

2.2.1.6 *X-ray photography.* A special application of continuous tone DTR materials is in X-ray photography. DTR methods are a very attractive proposition

in those cases in which the time factor is of the utmost importance. Moreover, the sensitivity peculiar to DTR materials enables very brief exposures to be given. The materials for X-ray photography differ from the DTR continuous tone materials in that the fluorescent and other ingredients are incorporated in the sensitive layer (more comprehensive details are given in chapter 5).

2.2.1.7 *Water-developable layers.* In carrying out experiments with sparingly soluble organic silver salts it was found that these compounds could be used in the manufacture of light-sensitive emulsions. The negatives thus obtained can be developed even in developing baths of very low concentrations.[3]

2.2.2 ONE-SHEET SYSTEMS. At the very outset, several attempts were made to design DTR systems using one-sheet materials instead of the two-sheet system in which the negative and positive had to be separated. In one-sheet systems both negative and positive layers are coated together on a single support.

There are three ways of constructing such materials. These have the same applications as the conventional DTR materials.

2.2.2.1 *Negative layer on top.* This method works in such a way that the negative layer is exposed and the material is then processed in a DTR developer. This results in the formation of a positive image in the bottom layer. There are two ways of rendering this image visible. In one of them the negative layer is simply washed off. If such materials are used, special precautions must be taken during exposure: it is necessary to expose with the aid of a reversal optical system, such as a right-angle prism in order to obtain a non-laterally reversed positive. Reflex exposure can only be carried out through the support, and in this case a transparent base made of a material with a low light-scattering coefficient has to be used.

The second method consists in the use of a completely transparent support thereby the image is viewed through the base after the reflex exposure. Either a strongly pigmented layer has to be interposed between the negative and the positive or the nuclei layer has to be dyed sufficiently strongly to mask the negative image. If these measures are not taken, the resulting contrast is too low (for details see chapter 4).

2.2.2.2 *Positive layer on top.* In this case also there are two variations.

In the first instance, the positive layer is left on the negative. In this case, the densities in the negative have to be masked by means of a white intermediate layer or by dying the positive. Reflex copying of duplex originals has to be done through the support or through the positive layer using a suitable optical system.

Another method consists in transferring the positive image to a separate sheet of paper, as described in many patents. The image can be transferred

either partly or completely. Transfer in part implies that several copies can be made. This variant can be regarded as a kind of two-sheet system.[4]

2.2.2.3 *Intargo material.* Another possibility, that of uniting the positive and negative on one base, appeared at the very beginning of DTR. It consists in coating a mixture of a very dilute light-sensitive emulsion and developing nuclei on to a transparent support. After exposure, this material is developed in a developer containing sodium thiosulphate. The silver in the exposed (negative) areas has a low covering power whereas that in the unexposed areas has a rather large one. This phenomenon is peculiar to the DTR system. The final contrast resulting from the difference in covering power of the two forms of silver represents the image (see chapter 6). The principle of bringing the nuclei into the emulsion layer was also applied in the "contour-film" of Gevaert Photo-Producten NV for textile printing purposes.

2.2.3 MISCELLANEOUS. In this section all the other systems which do not come into the category of the DTR systems mentioned above will be dealt with. They cannot be classified with either the one or the two-sheet systems.

2.2.3.1 *Deposition of nuclei.* A further means of simplifying the DTR process in such a way that only a negative material has to be used, consists in the deposition of nuclei on to a sheet of normal paper before or during processing and using the latter as positive. This can be achieved by adding the nuclei directly to the developer or by treating the negative or positive paper with a solution of nuclei just before introducing it into the developer tank in the apparatus. The negative is then moistened with developer solution and squeegeed on to the paper which is used as the positive. The success of such systems is determined by the stability and the keeping properties of the nuclei solutions in the presence of developing substances at high pH-values.[5]

2.2.3.2 *Stripping-out systems.* During experiments on DTR systems it was discovered that as a result of the silver deposit in the positive, the properties of adhesion between the negative and the positive could be also influenced.

These considerations led to the production of a material consisting of a negative covered with a nuclei layer and a "positive" consisting of a base, a gelatin layer and a binder layer in which a finely divided dye was dispersed. When, after exposure, both materials are placed in a developer-fixer and pressed together, a silver image is formed. This brings about a modification in the adhesion of the negative to the positive such as that after a short period of drying and subsequent separation of the materials, the dye layer remains adhering to the silver areas in the positive (non-exposed parts of the negative) and is transferred image-wise to the negative. This system was further developed

so that it could be used for the various methods of duplicating described in the following paragraphs.

(*a*) Spirit Duplicating. If the dye contained in the positive is soluble in alcohol, e.g. crystal violet, the negative can be used as the printing matrix for spirit duplicating after normal treatment. It should, however, be noted that "printing chemicals" still always have to be used in the actual printing process (for further details see chapter 5).

(*b*) Thermography. If the pigment employed is a dye which sublimates at a higher temperature, then, after the treatment described above, the negative can be used as the matrix in a thermographic printing process. In this case the negative and the printing stock are guided over a heated drum which causes the dye to sublimate and be deposited in the form of an image on the receptor (for further details see chapter 5).

(*c*) Offset Printing. It is also possible to use the pigment layer in the positive as the printing matrix in offset printing, such layers being very hydrophilic because of their strong tendency to swell. Some slight modifications must however be made to enable the pigment layer to be stripped off right down to the surface of the support. The latter is generally made of a hydrophobic material, which accepts ink. Before commencing the printing operation, the weak pigment layer is treated with a hardening solution to make it withstand the mechanical forces arising in the printing process.[6]

(*d*) Stencil systems. In another variant of the stripping system the pigment layer, after separation of the negative, is transferred to a sheet of Yoshino-paper to enable the latter to be used as the printing element in stencil machines. The decisive factor in this system is that the adhesion in the areas to be stripped out (non-exposed negative) must be greater than that of the pigment paper to the support so that the pigment layer can be stripped out right down to the support itself. On the other hand, the adhesion of the stripped-out pigment layer to the sheet of Yoshino-paper must be greater than that of the layer to the support, if the entire pigment layer is to make intimate contact with the sheet of Yoshino-paper. Only when this condition is fulfilled will good usable stencil matrices be obtained.[7]

2.2.3.3 *Light-sensitive nuclei layers.* Another variant of the DTR-principle is given by the use of light-sensitive layers of nuclei. Two ways of achieving this have been described:

In the first place a silver halide layer with a very low silver content (about 0·1 g/m^2) can be used for the nuclei layer after an image-wise exposure. This layer can be treated with water containing Phenidone as developing agent, together with an emulsion layer, consisting of organic silver salts (see 2.2.1.7). A complexing agent such as is used in the case of silver halide, is not necessary as the organic silver salts are sufficiently soluble in water. The silver then diffuses mainly (as a result of the diffusion gradient) towards those areas in the

positive in which developing centres were formed on exposure. In this way a negative of the original is obtained.[8]

The second method is as follows. In a layer containing zinc oxide and sulphur compounds, development centres can be created either by exposure or by reactivation of the existing centres by the addition of certain substances. If moreover, soluble silver salts are present in this layer or if a non-exposed silver halide layer is used as a source of silver, then after the exposure of a positive and processing it in a DTR developer, a negative can be obtained in the nuclei layer.[9]

2.2.3.4 *Electro-conducting silver images.* During the past few years much effort has gone into research and development with the object of elaborating systems which would enable printed circuits to be manufactured directly without having to resort to the time-consuming process of etching a photoresist/metal foil. It was found that in certain circumstances it was possible to obtain a positive silver image of sufficiently high conductivity with DTR systems. This image can be used in the manufacture of electronic units.[10]

2.2.3.5 *Polymer images.* A further application of the DTR system was discovered when polymer reliefs were made either for printing purposes or—when the layers were dyed black—for copying. The silver which diffused from the exposed and developed negative towards a positive which is covered with a layer of a monomer functions as a polymerization catalyst in the presence of traces of peroxide. After separation, the non-polymerized parts can be washed out and a legible positive relief of the original is then obtained.[11]

2.2.3.6 *Colour photography.* Various possible uses for the DTR technique in colour photography have also been discovered. Firstly in colour separation techniques the DTR-method provides a simple means of obtaining colour correction masks.[12] Secondly, the production of colour images by the negative/positive method using the dye-bleach process has been described.[13] Image reversal is achieved by DTR methods.

In this chapter we have attempted to give a short survey of the possibilities afforded by the relatively young DTR-process. The future will undoubtedly see further developments in the DTR process and there is also the prospect of other interesting applications being brought to light.

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III. THE OFFICE COPY

3.1 *Introduction*

Ever since mankind has used writing to record thoughts, words and information there must have been a desire to duplicate this writing. For thousands of years the only method available was that of the laborious copying of the documents by hand. This was the state of affairs until about 500 years ago when typography was invented, an invention which led to the wide dissemination of written documents. However, all manual processes for duplicating were found to be time-consuming and moreover involved the risk of copying errors. Therefore a search was soon made for methods of copying originals with the aid of light.

The first usable process was the blueprint process which was invented by Herschel,[1] this process is based on the conversion of ferric (III) into ferrous (II) ions under the influence of light. Simultaneously with this silver-halide photography began to make rapid progress. The possibilities offered by the latter process were soon recognized, and silver-halide materials for photocopying were rapidly developed. However, this copying process was cumbersome, since it involved developing, fixing, washing and drying, and remained dependent on the use of a dark room. The DTR-process brought about a tremendous change in all this.

3.1.1 HISTORY. The first practical use for the novel principle was to have been for making copies. From 1940–41 Gevaert Photo-Producten NV placed on the market a copying process under the name Transargo[2] which was used as described below.

A negative material was exposed in contact with the original to be reproduced. The non-light-sensitive positive material containing the necessary chemicals for the reaction (sodium thiosulphate and colloidal silver sulphide as development nuclei) and the exposed negative were immersed in a dish containing a developer and after a few seconds squeegeed together by means of a rubber roller. The unexposed and thus non-developable silver halide in the negative diffused in the form of a dissolved thiosulphate complex into the positive where it was reduced to silver on the development nuclei. After the positive had been separated from the negative, the not very attractive yellow colour of the silver image in the positive had to be improved by means of a selenium toning bath.

Although the process aroused much interest, it disappeared again from the market owing to difficulties occasioned by the Second World War. The manual method of processing precluded the possibility of rapid development in strongly alkaline baths since the materials had to remain in contact with the developers

for considerable lengths of time. The necessity of having to use a toning bath was an added disadvantage. The advantages of the new process over the conventional methods were not however adequate to guarantee the general use of the process.

In Agfa AG, as in Gevaert Photo-Producten NV, it was soon decided to use the DTR-process for copying purposes. A suitable processing apparatus was designed by Agfa AG and a patent was filed[3] (see 3.5). Further development was retarded by the war. In the meantime the patent position had become really difficult and in 1948 Agfa AG and Gevaert Photo-Producten NV signed an agreement which enabled both firms to commercialize the process. Once the mechanical processing of the DTR-materials had been made possible and the materials were available on the market in the form of Copyrapid (1949) or Gevacopy (1950), the process became a success. A photographic copying process which could generally be used outside the dark room was made available. Since the appearance of this process, which was the first real office copying process, many thousand millions of copies have been made by this method. A great many photographic firms all over the world now produce materials for this process (see 3.1.7).

The first usable processing apparatus under the trade name of "Develop" was marked by the Firm of Trikop[4] in Stuttgart. Shortly afterwards many other firms entered the market with apparatus for the DTR-process licensed by Agfa AG (see 3.5).

The first negative materials for the Copyrapid process contained the developing agents (hydroquinone and Metol). The processing liquid was an activator, a term which is nowadays generally used. This solution contained alkali in addition to sulphide, potassium bromide and other substances. Not until later were the developing agents incorporated in the developing liquid instead of in the negative material and for many years, the materials of various manufactures worked in accordance with this method. The developer combination of hydroquinone and Phenidone greatly improved the process by increasing the speed of processing (see 3.2.2).

However, in the most recent years this version of the process has again been discarded, i.e. the developing agents hydroquinone and Phenidone are again incorporated in the materials and the activator contains the alkali mainly in the form of alkaline salts such as trisodium phosphate or in the form of organic bases. The reason for this is that the processing liquid has better keeping properties since it can no longer be oxidized by atmospheric oxygen and only needs to be protected from evaporation and from a decrease in pH due to the taking up of CO_2 from the air (see chapters 3.2.5 and 3.4). A developing apparatus in which the processing liquid is allowed to run into a plastic bag when not in use, thus reducing the surface practically to zero, has proved to be most satisfactory (see 3.5). In recent years a further tendency is observed: the manufacturers have made great efforts to realize a process which is as dry as possible. Swelling

layers are transferred from the positive to the negative and the paper sheets are partly provided with the nuclei necessary for the physical development, and this is done during the actual manufacture of the paper. All these measures have been taken in order to obtain copies as dry as possible. Nowadays, materials such as Copyrapid-Dry are available: these materials can be regarded as being dry only a few seconds after processing (see 3.4).

3.1.2 OPERATION. For the production of DTR-copies no dark room is required. However, the copying apparatus in the office should not be exposed to direct sunlight or to an intense artificial light source (see 3.2.1).

For the preparation of DTR-copies the following materials are required in addition to the exposing and developing units (see 3.5), which are commonly built in one single apparatus:

1. the light-sensitive negative material,
2. the non-light-sensitive image-receiving material (positive material),
3. the processing liquid (developer or activator).

For use in offices the negative and positive are supplied either from their own packaging or from so-called sheet dispensers which will deliver a sheet simply by pushing or pulling. The processing liquid is contained in the developing apparatus (see 3.1.1 and 3.5). The various stages in the production of a DTR-copy, namely the exposure of the negative to the original, the development of the negative and transfer of the unexposed silver halide to the positive, and the separation of the negative from the positive, will be described in detail below.

3.1.3 THE EXPOSURE (exposure latitude, detail rendering). For the exposure of the negative all the methods commonly used in photography can be employed: optical copying by means of a camera, print-through or transmission copying and reflex copying. However, apart from a few exceptions, reflex copying[5] is used practically exclusively. It offers the additional advantage of being able to make copies of double-sided originals, without the use of optical equipment. Use is made of a universal flat-bed printer in which the negative is placed, emulsion side upwards, on a glass plate and the original is placed with the side to be copied in direct contact with the emulsion layer. In order to guarantee close contact between the original and the negative sufficient pressure should be applied. Exposure is made from the back surface and through the emulsion layer of the negative. A developable latent image is now produced by the light reflected from the original (from the white areas), whereas the amount of light passing through the emulsion layer and not reflected (from the image-areas in the original) may not reach the sensitivity threshold of the negative material.

If it is assumed that the white areas in the original reflect the light ideally (100%) and that the black areas of the original reflect no light at all (0%), then the exposure of the negative emulsion layer in the areas corresponding with the

white areas in the original will be twice that ($\Delta \log It = 0{\cdot}3$) of the primary exposure produced by the light passing through the negative (see Figure 3.1). In practice, the white areas in common originals reflect only about 70% of the light and even the black areas still reflect about 6%. Therefore, the exposure difference in logarithmic values is only $\Delta \log It \simeq 0{\cdot}2$.

In order to be able to take advantage of this relatively small exposure difference, emulsions of sufficiently steep gradation must be used. It has been

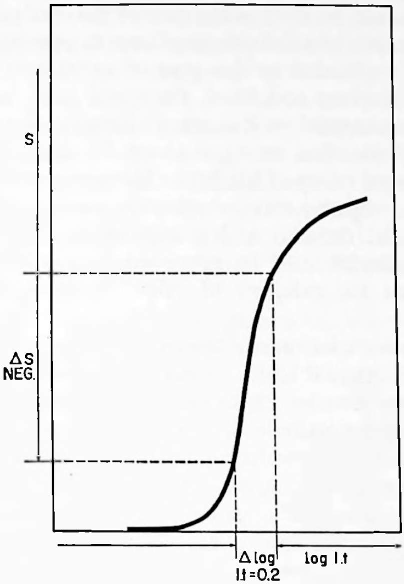


Fig. 3.1. Characteristic curve of reflex copying material.

found expedient to sensitize the emulsion to the yellow-green region of the spectrum since, in general, the gradation is steeper in the sensitized region than in the region of natural sensitivity (blue). Moreover, scattering of the yellow-green light of longer wavelength in a negative paper is smaller than that of the blue light so that toned areas are reproduced as uniformly covered areas. If the exposures were made with blue light only, such areas would be reproduced as discontinuous areas. Therefore, the exposure apparatus is provided with a yellow filter or with light sources e.g. green fluorescent lamps which radiate mainly in the region of sensitization of the emulsion. It is obvious that, for a reflex exposure to be given, the paper base of the negative material must be of uniform opacity.

Besides flat-bed printers, rotary printers are also used. With these, only single sheets and no books or journals can be copied. Here again the exposure is mostly carried out by the reflex method and to this end the negative and the original are laid on top of each other as described above and led mechanically past a light-source.

Negative materials of different speeds are manufactured. Although this is of no importance for the DTR-process itself, these materials are formulated in such a way that exposure apparatus can be used. In principle, negative materials of any speed whatever can be used in the case of flat-bed printers, whereas with rotary printers, negatives of a definite speed have to be used owing to the limited amount of variation afforded by this type of apparatus. The most common speed ratings are Medium and Slow, the speed ratio being about 1:2. In addition, a negative material with a speed rating of Normal (e.g. Copyrapid CRN) is also supplied. This rating is about 2·5 times as fast as a negative material with the speed rating of Medium. Moreover, the Copyrapid materials include a high-speed negative material which is used for exposure by projected light (exposure in the camera) and is suitable for making enlargements or reductions. This material must be processed in a dark room and therefore does not come into the category of office materials; it is dealt with in 3.2.1.

Although the exposure latitude of the negative is relatively large it is dependent on the type of original to be copied. When an original with details of different size is given a reflex exposure using different exposure times, it is found that the exposure latitude for medium-sized details is about $\pm 20\%$. When the exposure time is reduced, characters and signs are reproduced thicker than they are in the original. With further reduction in the time of exposure the background of the copy darkens, and the reverse is true when the time of exposure is extended, when characters and signs are reproduced thinner than in the original and when too long an exposure is given some of the details are no longer reproduced.

This is illustrated by the examples of reproductions obtained in various exposure experiments (Plate 3.1).

In all of the seven exposure tests the medium-sized and large characters are easily legible. The small characters on the contrary are too thick and partly blurred in the case of a 20% under-exposure, and too thin or only partially reproduced in the case of a 25% over-exposure. However, even with a 35% over-exposure or a 25% under-exposure the large characters in the reproduction are still legible in the reproduction.

The chemical aspects of these findings will be explained below.[6] Normally, it would be assumed that when a negative is given the correct exposure any detail whatever in the original would be reproduced somewhat thicker in the positive, since diffusion of silver salts can occur in all directions. However, experiments have shown that the details reproduced in the positive are somewhat

thinner than the corresponding details in the negative of the original. This can be explained as follows:

In the developed negative the details, in the form of silver halide, are practically completely surrounded in the border areas by reduced silver. When the silver halide is dissolved by the sodium thiosulphate, the silver complex will diffuse mainly into the silver zone since in these areas no soluble silver salts are present. However, the dissolved silver complexes emanating from the centres of the details will diffuse mainly into the positive layer, which is in the closest proximity, where they are reduced at the site of the nuclei so that the concentration of the silver complex is simultaneously lowered, thus promoting diffusion in this direction. Therefore, in the positive, the concentration necessary for the reduction of the silver complex is first reached in the centres of the details and thus the silver complexes diffuse mainly towards the centres of the details. At the edges of the details on the contrary, the required concentration of silver complex necessary for reduction to take place is by no means reached. The lateral diffusion of the silver salts in the negative as well as the diffusion towards the centres in the positive results in a narrowing of the details in the positive as compared with the details in the original. This has a favourable effect on the sharpness of the image.

The reproduction of colours in the original is broadly determined by the sensitization of the negative. In general the emulsions are sensitized orthochromatically to give a maximum between 530 and 550 nm. Thus with the exception of bright yellow which is only reproduced when the material also has been sufficiently under-exposed, all colours are satisfactorily reproduced as black in the positive. This is of advantage in office copying processes since it enables originals with a yellow background to be copied, and moreover DTR-copies of old, yellowed originals show black image areas on a clear, white background.

When copying originals with a coloured background by the reflex method, in most cases the exposure time should be increased, since the reflecting power of a coloured background is lower than that of a white background: otherwise, the DTR-copy obtained would have a fogged background. When exposing black writing on a red background, e.g. in the case of certain forms or pink typewriter copies the exposure should be lengthened by at least 20%. When the difference between the red and black densities is too small such an original can no longer be copied. When using a negative with an emulsion layer which is not sensitized to the red region of the spectrum, the red background areas in the original are reproduced as black areas in the positive.

Originals (e.g. typewriter copies on thin paper) which might give rise to difficulties when using the reflex method of exposure are preferably exposed by the transmission or print-through method. For this purpose, the typed copies should be single sided and the paper sufficiently transparent. With the print-through method, the image side of the original is placed in contact with the emulsion side of the negative and exposure is made through the back surface

of the original. It is self-evident that in the case of transparent originals, e.g. transparencies, this is the only possible method of exposure.

3.1.4 DEVELOPMENT. After exposure, the negative is placed on the positive with its emulsion side facing the image-receiving side of the positive. Both sheets are then introduced into two adjacent slots in the developing apparatus which is filled with a developer or activator solution. The sheets are uniformly pushed up to a pair of squeegee rollers, which transport the sheets and eject them from the processing liquid. When the positive and negative, pressed together, leave the apparatus in a slightly moist condition, it is necessary to wait for about 10 seconds before peeling the sheets, apart, commencing preferably from a corner of the sheets. It is advisable to separate the sheets at the same speed as that at which the materials are guided through the apparatus to enable a silver image of uniform density to be obtained over the entire surface of the positive. After a short time of drying the positive is ready for use, whereas the negative is usually discarded.

The developing apparatus should comply with certain conditions if optimum development of the negative and satisfactory diffusion transfer into the positive are to be achieved. When passing through the apparatus, the positive and negative material should absorb the least possible amount of the processing liquid. This amount depends on the distance through which the paper passes in the liquid before being nipped by the pair of rollers, as well as on the speed with which it is passed through the bath. Most of the developing apparatus available on the market have an immersion distance of about 10 cm and a travelling speed of about 8 seconds per 30 cm (see 3.5). The copying materials now available on the market will, however, also give satisfactory results with apparatus with reduced or increased travelling speeds or smaller or larger distances of immersion. The processing optimum nevertheless lies approximately at the values given above. These values are a measure of the industrial progress which has been made. In fact, in 1949, the first Copyrapid materials required an immersion distance of about 14 cm, travelling speeds of about 20 seconds per 30 cm in addition to which the positive and negative had to be kept in contact for about 30–60 seconds.

The development of the negative as well as the diffusion transfer process depend on temperature. In general the materials are designed in such a way as to give the optimum results at room temperature. When the processing liquid is at too low a temperature, the development of the negative does not take place sufficiently rapidly so that in some circumstances positives with a fogged background are obtained. On the other hand when the temperature of development is too high, all the stages in processing are accelerated, with the result that more processing liquid is taken up and the copies turn a deeper yellow afterwards; thus, in some circumstances, the stability of the image is impaired (see 3.3.1 and 3.3.2).

3.1.5 MULTIPLE COPIES

3.1.5.1 *Two copies.*[7] It is possible to prepare more than one copy from a single negative, this means that the unexposed silver halide must be distributed over two or more positives. This is difficult to realize in practice when the silver halide solvent (sodium thiosulphate) is present in the processing liquid, and is therefore ruled out in this case. When however the sodium thiosulphate is present in the positive the process is the same as that described for the single-copy process, with the difference, however, that the sheets which have been pressed together are peeled apart, starting from the upper end, before the lower end has left the pair of nip rollers. In order to obtain a uniform image the positive and negative are separated from each other at approximately the same speed as that at which they are passed through the apparatus. With these short times of contact, only part of the soluble silver complexes diffuses into the positive. The negative together with a fresh positive is run through the apparatus once more and after remaining in contact for about 30–40 seconds a second copy of good density is obtained. In this way the soluble silver complexes of the exposed negative are distributed over two positives. The equality of the two copies depends largely on the method of processing but with a certain amount of skill, this can easily be controlled. For two or more copies the negative should be slightly under-exposed by about 10% less than the normal time in order to increase the amount of silver halide available for transfer to the positive. Preliminary exposure of the negative by daylight or artificial light should be avoided as otherwise the second copy will be too low in contrast.

3.1.5.2 *Multiple copies.* In general, it is not possible to obtain more than two copies from a single negative, when the DTR-positive contains a silver-halide complexing compound (such as sodium thiosulphate in the image-receiving layer). Therefore, when more than two copies are required from one original, special positives, such as Copyrapid-Multi Positive, which does not contain any sodium thiosulphate are used. With the normal negative material and a special positive material, five and with a certain amount of skill even up to ten copies can be made. It is obvious that the image-contrast in the positives will decrease gradually with increase in the number of copies produced. If a negative with the customary coverage of 1 g of silver per sq m would be used with the intention of distributing this quantity of silver between 5 positives, then only about 0·2 g of silver per sq m would be available for each positive. In practice this value is even much lower since considerable amounts of the soluble silver salts are not available for transfer to the positive. Indeed, part of the silver halide remains as fog in the negative, and soluble silver complexes are dissolved in the bath or diffuse into the paper support of the negative. In the case of office copying a good yield of silver in the positive is about 60%.

The positive materials for multicopying now available on the market (such

as Copyrapid CRMP) contain no sodium thiosulphate. This also holds for the processing liquid which contains no, or only very small amounts of sodium thiosulphate. The solution and complexing of the unexposed silver chloride in the negative is brought about by the high sodium sulphite content of the processing liquid. Since the silver halide is dissolved much more slowly by sulphite ions than by thiosulphate ions, it is possible to transfer the silver complexes formed to more than one positive.

In the patent literature many widely differing methods have been described for preparing multiple copies by the DTR-process.[8] Only a few of these have established themselves in practice, whereas others have disappeared again from the market. For instance, in 1960 Gevaert Photo-Producten NV, Antwerp, introduced a multicopying process by means of which more than ten easily legible copies could be obtained from a single but special negative. However, this process forced the customers to carry a double stock of materials, namely normal office copying materials and materials for multicopying. For this reason the special negative material was withdrawn from the market, notwithstanding the many advantages which result when multiple copies are prepared from a single negative on a "double-weight" base.

In principle, the method of preparing multiple copies is the same as that described for the preparation of two copies. The negative which has been given a somewhat short exposure is passed repeatedly, each time with a fresh positive material, through two separate slots in a developing apparatus. The time for which the negative and the various positives are left in contact depends not only on the developing apparatus used but above all on the number of copies required. For instance, when two copies are required a time of 15 seconds for each would be correct, whereas in the case of 3 copies the time would be 10 seconds for each copy and for 5 copies about 5 seconds. In any case, it is advisable to leave the last positive in contact with the negative for 30–60 seconds since all of the residual transferable silver halide then becomes dissolved and the last copy acquires a higher image density.

Since a normal negative, on a base weighing 80 g per sq m becomes really flabby after it has been passed repeatedly through the apparatus it can be of some assistance to support the negative with a sheet of material which has already been processed and discarded. This greatly facilitates the preparation of a large number of copies.

3.1.6 SPECIAL POSITIVES. Various manufacturers supply DTR-positives with special properties; these include positives on a heavy paper base. Normally, the paper base used for office copying materials has a weight of 80–90 g/sq m. The various coatings applied raise the weight to about 100 g per sq m. A copy of size A-4 (21 cm × 29·7 cm = $8\frac{1}{4}$ inches × $11\frac{3}{4}$ inches) weighs between 6 and 7 g.

Positives on light-weight paper bases (about 50 g per sq m) are also available

e.g. for the preparation of airmail copies; a copy of size A-4 weighs only between 3 and 4 g. It is possible to provide positives on a still thinner paper base but this would lead to serious difficulties in manipulation during processing. However, for many years a very thin positive material specially designed for airmail purposes and having a weight of only 1·7 g for a copy of size A-4 was available on the market.[9] To enable such thin positives to be handled in the developing apparatus, they were provided with thick temporary supports. After processing and removal of the negative material, this temporary support was separated from the permanent one. This was the lightest photographic paper available in the world.

For the preparation of index cards or for similar purposes a positive on a strong cardboard base (250 g/sq m) is available. In this case a copy of the size A-4 has a weight of 16 g. It should be mentioned that it is advisable to rinse copies which are intended for archival purposes in order to guarantee that they will last for several decades.

It is also possible to prepare double-sided copies. For this purpose special positive materials which are coated on both sides are used. The double-sided positive is sandwiched between two negatives, each of which has been given a reflex exposure to one side of a double-sided original. The three sheets are then fed into the three slots of the developing apparatus, the positive material being fed into the centre-slot. When the three sheets emerge pressed together from the apparatus, they are left in contact with each other for a while and the negatives are then stripped off, one after the other, from the positive. Apparatus with only two guiding slots are not suitable for the preparation of double-sided copies (see 3.5).

The transparent types of positive materials supplied by various manufacturers, also play a prominent part in practice. The materials are coated on to a transparent film base, on to matt film or on to paper which has been rendered transparent. With these positive materials the normal single-copy process is used. However, in order to obtain a sufficient density of 1·5 to 2, the positive should be kept in contact with the negative for a longer time (about 1 min). During transfer, the sheets which are pressed together tend to curl, with the positive sheet on the inside. In fact when the materials are moistened in the developing apparatus, the paper base of the negative swells to a much greater extent than does the hydrophobic base of the positive.

Any attempt to prevent curling, involves the risk of the negative coming away from the positive sheet so that in the areas of loose contact no transfer of the positive image takes place. The transparent positives should be rinsed for several minutes and then dried. They are used for projection purposes, for the preparation of blue-prints and for photomechanical transfer.

For producing transparent copies on film base, some Japanese photographic firms market special negatives on a lacquered paper base. During development, these negatives possess sufficient dimensional stability to prevent the above

mentioned curling from taking place. In this connection it should be mentioned that particularly in Japan, relatively large numbers of transparent positives are used for making further copies by means of the cheaper diazo process. In order to reduce the drying time of the transparent copies, they are often passed into an alcohol bath (preferably methanol) after having been separated from the negative. For instance an apparatus, which is filled with methanol instead of developer is provided in addition to the developing apparatus.

Many years ago, coloured positives on supports (yellow, green, blue, pink) were also available on the market, but nowadays they are in general no longer supplied because the demand is too small. When coloured positives are required for certain purposes it is possible to incorporate dyes* in the developer, so that the entire positive is dyed on processing.

3.1.7 MANUFACTURERS AND TRADE NAMES OF OFFICE DTR MATERIALS AVAILABLE ON THE MARKET. The number of office copying materials which are based on the DTR process and which are nowadays available on the market and supplied by various manufacturers is quite impressive. It is not our intention to give a comprehensive list of the different kinds of negative and positives available since this is beyond the scope of this book. A list of the most common manufacturers and the trade names of their materials is given in Table 3.1.

3.2 *Materials*

3.2.1 THE NEGATIVE.[10,11] (Composition and processing.) DTR negatives for use in office copying employ silver halide emulsions almost exclusively. The emulsions which consist entirely or substantially of silver chloride, may sometimes contain small amounts of silver bromide and occasionally traces of silver iodide. Moreover, several other substances may be added to the emulsions. These substances exert a favourable influence on such photographic properties as density, image-tone, gradation and fog value[12] as well as on the transfer properties.[13,14]

3.2.1.1 *Sensitivity of the negative.* For the various fields of application of the negative, several types of material of different speeds are available. For office copying there are materials of low, medium and normal speed (cf. 3.1.3). For making enlargements or reductions using a reprographic camera a correspondingly highly sensitive type is available.

This highly sensitive negative is sensitized to longer wavelengths and has an absorption maximum at 550 nm. Its gradation is somewhat softer than that of

* The following dyes are suitable for this purpose and used in amounts of from 2–5 g/litre:

red	:	eosine
orange	:	fluoresceine
yellow	:	supranol yellow R
green	:	supranol yellow R + acilan fast green 3 G
cyan	:	acilan fast green 3 G

TABLE 3.1
MANUFACTURERS OF DTR MATERIALS

Manufacturer	*Trade Name*
Agfa-Gevaert formerly Agfa AG (Germany) and Gevaert Photo-Producten NV (Belgium)	Copyrapid Copyrapid Gevacopy
American Photocopy Equipment Co. Evaston, Illinois 60202, U.S.A.	Copy Quick
Anken Chemical & Film Corp. Newton, New Jersey 07860, U.S.A.	Transcopy
Fifa S.A. Argentina	Fifacopia
Forte Photochemical Industry Vâc, Hungary	Copyfort
Fotochema Hradec Cralove Czechoslovakia	Fomacopy
Fotokemika Zagreb, Yugoslavia	Samocopy
Fuji Photo Film Co. Tokio, Japan	Neocopy
R. Guilleminot Boespflug & Cie Paris, France	Copyguil
Haloid-Xerox Inc. Rochester, U.S.A.	Haloid-Texta-Copy-Paper
Interchemical Corp. New York, U.S.A.	Icinstant Copy Paper
Kodak Ltd. London W.C.2, England	CT-Paper Instafax
Mitsubishi Paper Mills Tokio, Japan	Hishi Rapid
Orbi Ltd. Tel Aviv, Israel	Orbikopirapid
Ozalid/General Aniline & Film Corp. Binghampton, New York, U.S.A.	Transferon
Peerless Photo Products Inc. Shoreham L.I., New York, U.S.A.	Dristat
Samun Vienna 19, Austria	Austronkopie
Tensi S.p.A. Milan, Italy	TCT Long Life
Yorktown Industries Inc. Chicago, Illinois, U.S.A.	Universal PTX

the less sensitive types, and it can only be processed in red light in a darkroom. Processing is carried out in the same type of apparatus. Owing to its higher sensitivity, the emulsion is also more coarse-grained. The transfer consequently requires somewhat longer times of contact, e.g. 15 to 20 seconds instead of 10 seconds, since in this case the coarse-grained silver halide is developed more slowly and is dissolved in a more complex form by the thiosulphate.

Since originals are generally printed on both sides, a reflex exposure is usually necessary for the production of an office copy. Consequently, the layers must be sensitized, particularly to yellow or yellow-green light. Negative layers which are only sensitive to blue light scatter light too strongly and yield unsharp

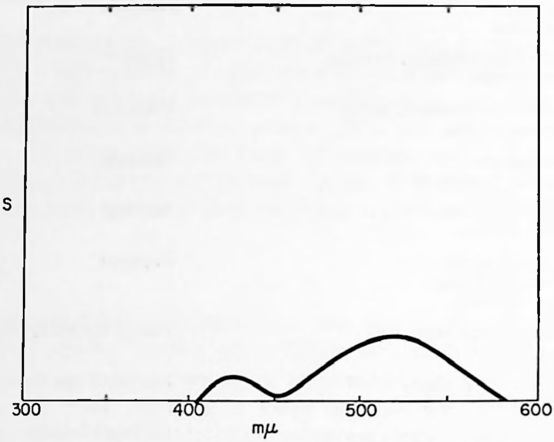


Fig. 3.2. Material with the narrowest range of sensitation is used when reproducing coloured originals.

prints of low density. Moreover, the more or less strong structure of the base becomes more obvious in blue than in yellow light, and this has an important bearing on image sharpness and on the uniformity of the prints. Finally, this region of sensitization proves to be particularly suitable for copying originals which, in offices, usually take the form of a text or original drawings. A yellow text on a white background presents only a weak contrast in colour. Since originals of this kind are quite rare, any difficulties which are likely to arise in making copies of such coloured originals are seldom encountered.

In order to match this sensitization range, the exposure of the negative should be made using yellow or yellow-green light. The best way of keeping colour defects in the reproduction of coloured originals to a minimum is to use the narrowest range of sensitization (cf. Figure 3.2).

Difficulties arise in the use of silver-bromide emulsions because the bromide ions originating from the development of the negative, hinder the reduction of the dissolved silver salts at the site from the nuclei.

More rapid processing of silver bromide layers can be accomplished e.g. by the addition of a silver chloride emulsion. The silver chloride is converted into silver bromide by the bromide ions which have originated during the development of the negative. Only in the unexposed areas does the silver chloride remain in an unaltered form: it dissolves more readily than the silver bromide and diffuses more rapidly to the positive layer.[15]

3.2.1.2. *Stability of the negative in daylight.* The medium and low-sensitive DTR negatives can be processed in subdued daylight. Direct sunlight should be avoided. The fact that processing can be carried out in daylight has been the deciding factor in the adoption of this process in offices.

In order to make the negative sufficiently insensitive to daylight, yellow dyes, viz. the so-called screening dyes, are added to the negative layer. Owing to their inherent absorption, these yellow screening dyes reduce the sensitivity to blue light of the negative and consequently reduce the natural sensitivity of the latter to daylight and artificial light, which is known to contain a large proportion of blue light.

Yellow, non-diffusible, pigments are used as screening dyes. If the negative has to be used afterwards, soluble screening dyes, which can be decolorized in the alkaline developing liquid or washed out, can be employed.

By adding substances, which absorb in the blue short-wavelength region of the spectrum, the negative is largely protected from any ultraviolet radiation which may fall on it during processing.

3.2.1.3 *The silver content of the negative, and silver transfer.* The silver content of the negative plays a decisive role in the production of a positive of sufficiently high maximum density. With the maximum coverage, the quantity of silver transferred to the paper positive varies between 0·4 and 0·5 g per sq m. This can be attained with a minimum silver content of 0·8 g per sq. m in the negative when an ordinary photographic paper on a raw base is used, since, in general, only approximately 40 to 60% of the silver in the negative is deposited in the positive in the form of image silver. Most of the remainder of the dissolved silver salts diffuse into the raw paper base, only a small part of it remaining in the sensitive layer. The concentration of the thiosulphate relative to that of the dissolved silver salts which are still present rises with increase in the reduction of the silver salts and this results in the formation of higher thiosulphate complexes which contain less silver and which are reduced with greater difficulty.

Since the silver deposited in the positive layer has a large covering power on account of its fine grain, amounts of 0·3 g of silver per sq m are already sufficient

to attain a reflection density of 1. In a coarse-grained negative, however, 1 g of silver per sq m is necessary.

When paper supports laminated with plastics are used for the negative base, or again, when the latter has been rendered impervious to water by a special treatment,[18] the silver content per sq m in the negative can be diminished to 0·3–0·5 g. In this case almost all the silver in the negative is transferred because on the one hand none of the negative emulsion can sink into the paper base and because on the other hand no silver salts are retained by adsorption by the paper base.

The silver content of the negative is not, however, the only factor which controls the density of the positive. A large number of variables has an important influence, i.e. the blue-toning agents used and the stabilizing agents, which are preferably added to the developer solution and/or to the positive, the absorption and swelling properties of the negative and the positive material, the sodium thiosulphate content of the positive layer, and the depth and density of the deposit in the positive. Even if the silver content of the negative is sufficient, individual factors may impair the transfer of silver to such an extent that a satisfactory density can no longer be obtained. An exact evaluation of the negative, positive and developer solution is thus absolutely essential if a satisfactory density is to be obtained.

The rapid transfer of silver is governed by the swelling properties of the negative layer in much the same way as it is by those of the positive. The binding agent in the negative layer is comprised almost exclusively of gelatin. The addition of hardening agents decreases the swelling power of the gelatin layer to such an extent that development still takes place rapidly and completely, whereas, at the same time, the path of diffusion to the positive is shortened by the diminished swelling of the negative. Consequently, the speed of transfer is increased. Too strong, a hardening of the negative layer should of course be avoided especially as it may impair the efficiency of contact.

3.2.1.4 *Development of the negative.* For the satisfactory and rapid development of the negative, the presence of developing agents in the negative layer as well as the use of an active processing solution maintained at the right temperature are advisable.

A mixture of hydroquinone and potassium metabisulphite is therefore used, inasmuch as the developer solution still contains developing agents (cf. 3.2.5). The potassium metabisulphite stabilizes the hydroquinone. If Phenidone or other developing agents are added to the negative emulsion, they can be omitted entirely from the processing liquid[17,18,19,20] (cf. 3.4).

3.2.1.5 *Gradation of the negative and processing latitude.* For reflex copies a particularly steep gradation of the negative must be arrived at since the passage of light twice through the emulsion inevitably results in a softer positive image.

The present emulsion techniques enable emulsions of very steep gradation to be prepared.

As an example of an office copying DTR material, a Copyrapid negative has a gamma value of approximately 4 after reflex exposure and suitable processing while in contact with a Copyrapid positive. This gamma value is even increased to approximately 6 on being transferred to the positive. The typical shape of the gradation curves is shown in Figure 3.3.

The same relations apply to negatives of low sensitivity. With negatives of high sensitivity, which, as mentioned before, are used mainly for reproduction

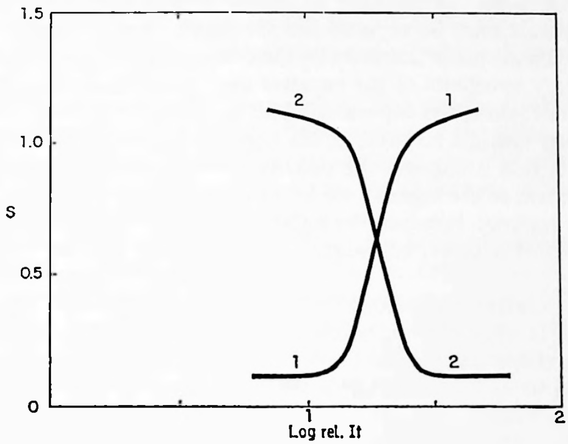


Fig. 3.3. Gradation curves of a Copyrapid negative (1) and a Copyrapid positive (2) developed while in contact with each other.

purposes using a reprographic camera, such steep gradation is sacrificed in order to obtain good continuous tones.

The gradation of the negative also bears an important relation to the exposure latitude, normally the steeper the gradation, the lower is the exposure latitude. Since on the one hand, the density decreases with decrease in the steepness of gradation and with any shortening of the predetermined times of contact and since on the other hand the risk of fogged high-lights (fog in the non-image areas) increases considerably simultaneously, a compromise has to be made here. The exposure latitude, which naturally depends on the tone range of the original, is made such that in practice it averages 20%. Within this range a good density and highlights free from fog are obtained with materials of sufficiently steep gradation.

The composition of and the method of processing the negative are selected in such a way that with the above-described exposure the latitude of approximately 20%, at temperatures ranging from 18 to 30°C for the developer and times of contact of from 5 and 90 seconds, satisfactory prints are obtained.

3.2.1.6 *Stability and keeping properties of the negative.* The sensitivity of the negative depends on different variables. In fact, the sensitivity of a negative can drop during prolonged storage or as a result of too great a hardening of the negative layer which is composed substantially of gelatin.[10,11,21] Moreover, the sensitivity of the negative depends on the temperature of the layer during exposure; i.e. when the exposure apparatus is used repeatedly, and becomes hot, the exposure must be adjusted and shortened. Any changes in the time of exposure which are made necessary by the heating up of a layer are independent of the primary sensitivity of the negative used as well as of the colour of the light used for making the exposure (white or yellow).

Finally, any residual moisture in the negative has a certain influence on the sensitivity, in that it changes the opacity of the paper base. The higher the moisture content of the negative the lower is the opacity of the base. The dryer the negative material, however, the higher is its opacity, and hence the necessity to give a somewhat longer exposure.

3.2.2 THE POSITIVE MATERIAL.[22,23,24] (Composition and functioning.) The positive layer in office copying materials, that is to say the one which serves as the image-receiving layer, should satisfy the most exacting requirements. Such layers should be as thin as possible when dry, they should swell rapidly and strongly in the developer and be capable of making close contact with the negative material. They should not, however, adhere too strongly to the latter: in other words, the negative and positive materials should not stick together for the first few minutes. Moreover, the swelling properties of the positive layer should be such that the transfer of silver takes place efficiently and with sufficient rapidity. In fact, sharp images (without diffusion halation) of sufficient density and in spite of the short transfer time of 5 to 10 seconds, are only obtained if the dissolved complex silver compound diffuses rapidly enough from the unexposed image areas of the negative into the positive layer where it is reduced to image silver on the nuclei.[25] On the other hand, the amount of developer absorbed by the positive layer should not be too high otherwise staining of the white background areas by developer oxidation products is likely to occur (see 3.3.1).

3.2.2.1 *The development nuclei.* The development nuclei[22,24] form the essential constituents of the image-receiving layer and are applied to the base together with binding agents which are either soluble in or are capable of swelling in water. These binding agents function as a protective colloid for the nuclei and,

in addition, owing to their swelling properties, favourably influence the transfer process and ensure good contact between the positive and negative layers.

In the presence of alkali and developing agents, the silver halide which has dissolved in the form of a complex from the unexposed and therefore undeveloped image-areas in the negative and has diffused into the positive, is deposited as image silver on the development nuclei.

The quality of the copies obtained largely depends amongst other things on the type, amount, and size of the nuclei used. Nowadays, heavy metal sulphides[25-33] or heavy-metal selenides, more particularly silver sulphide, nickel sulphide, mercury sulphide, or palladium sulphide are used in preference to colloidal metal nuclei for the development nuclei,[23,31] on account of their better stability and higher activity.[33] In a separate section (see 3.2.3) the correlation between the type of nuclei, conditions of preparation and activity is described.

3.2.2.2 *Binding agents for the positive layer.* The transfer behaviour of the positive layer largely depends on the binding agent or on the mixture of binding agents used, the swelling properties of which agents strongly influence the speed of transfer, the blackness of the image areas, the uniformity of the deposited silver and the adhesive power of the layer.

Suitable binding agents for the image-receiving layer are substances which are either soluble in or are capable of swelling in water, such as gelatin[23,34] used alone or in combination with alginic acid derivatives,[35,36] polyvinyl acetate, polyvinyl alcohol,[37] starch and starch derivatives,[38,39] cellulose derivatives, particularly carboxymethyl cellulose, or gallactomannans.[40]

Synthetic binding agents such as copolymers of polyvinyl ester and maleic anhydride[41,42] or mixtures of water-soluble polysaccharides and multivalent alcohols[43] can also be used. As a matter of fact choice of the right mixture is all-important.

The water absorptivity of the positive, and thus indirectly the white image areas as well as the image tone can often be influenced by adding certain synthetic polymers. The very important part played by the swelling properties of the positive layer in influencing image quality lies in the actual principle on which the DTR-process is based. In fact, if the layer swells too slowly, the entire DTR-process is retarded. The silver is deposited from a too small concentration of silver and the density is too low and when the times of contact are short a brown-coloured image may even be formed. On the other hand, the positive layer should not swell too strongly since in this case the distance through which the diffusing substances have to pass is considerably increased, thus lengthening the times of transfer and contact.

It should also be mentioned that, depending on the choice of binding agent, the positive and negative layers tend to stick together when the time of contact becomes too long. With suitable combinations of binding agents such as starch or starch ethers[39] as well as gallactomannans[40] it is possible to prepare layers

which have good transfer properties and which can be separated even if they have become completely or almost completely dry. In certain circumstances, the binding agents should be coated either on their own or mixed with other binding agents to form a separate layer on top of the nuclei layer in the positive.[40]

3.2.2.3 *Composition of the image-receiving layer of the positive.* The first positives used for office copying[23,25] were those in which the image-receiving layer took the form of a gelatin layer applied to a paper base and contained colloidal silver sulphide as development nuclei and an organic mercapto compound, e.g. mercaptobenzthiazole as image-toning agent. The developing agents and the silver halide solvent necessary for the process were present in the alkaline developing liquid with which the exposed negative material and the positive material were moistened.

Most of the DTR-positive materials now available on the market are composed of two[44] or even three layers and a further layer which has special functions may also be present either on top of or underneath the nuclei layer in which the actual image is formed. The layer coated on top of the nuclei layer which itself contains no nuclei but exhibits good swelling properties and otherwise has the same composition as the nuclei layer serves mainly to ensure good contact between the negative and positive material during transfer and thus the production of good and uniformly black image areas. Moreover, after drying, this layer provides a protective coating for the image layer, thus preventing erasure of the copy. In addition, matting agents such as colloidal silicic acid[45] aluminium silicate, aluminium oxide or other pigments can also be incorporated in this layer to prevent silver from being deposited in the large areas in the form of glossy metal mirrors (bronzing or plumming of the black image areas). Bronzing of the positive image occurs when the silver deposited protrudes from this surface, e.g. when thin layers containing a large quantity of nuclei are used (bronzing disappears when the surface silver is oxidized). Of course, in practice only the above described expedient of applying a supercoat to the nuclei layer can be considered.

The baryta layer[46] under the nuclei layer in most DTR-positives consists mainly of barium sulphate as white pigment dispersed in a binding agent—usually gelatin—which is water-soluble and is also capable of swelling in water. This layer may also contain alkali-neutralizing compounds (see 3.3), optical brightening agents and dye pigments, indicating that the baryta layer is used to form the white background areas in the positive. Moreover this layer gives the copy a glossy appearance and regulates the water content of the positive during and after transfer. The functions of the baryta layer are given in more detail in section 3.3.1.

In principle, it is also possible to dispense with the use of a distinct positive layer, i.e. when the nuclei are present in the paper base itself,[47,48] and the negative layer is made to acquire the requisite swelling properties to maintain

adequate contact between it and the image-receiving material during the DTR-process. However, such materials have not yet found acceptance on the market because of their poor quality.

3.2.2.4 *The silver-halide solvent* (its purpose and manner of functioning in the developer and in the positive). The silver-halide solvent[25] which is generally used for carrying out the DTR-process and which is almost exclusively sodium thiosulphate, can be present either in the developer or in the positive layer. These systems have their advantages as well as their disadvantages.

When developers containing sodium thiosulphate are used, large amounts of silver halide are dissolved from the negative before the negative comes into contact with the positive and are therefore lost to the transfer itself. The silver thiosulphate complexes formed are gradually reduced by the developer thus forming a black silver sludge which darkens the developing liquid and soils the developing apparatus. In addition, the calcium and magnesium salts which have been partially dissolved and rubbed off mechanically from the positive layer and the paper base are also deposited in the developing liquid in the form of flocculent hydroxides or carbonates. The reduced silver tends to become adsorbed to these flocculent deposits, the dark sludge which is precipitated being usually very voluminous. Quantitative measurements have shown that a sludge of 100 ml in volume contains only a few milligrams of solid.

These losses in silver and the heavy staining of the developer accompanying the solution of the silver halide from the negative can be greatly reduced by incorporating the sodium thiosulphate necessary for the DTR-process, in the positive layer. However, the success of this measure is dependent on the rapid drying of the positive layer, in order to prevent the sodium thiosulphate as well as other possibly highly soluble substances from diffusing into the paper base in which, some months later, the sodium thiosulphate may decompose, thus causing a strong, partially stained yellowing of the copies to take place.*

The above described baryta layer under the nuclei layer also prevents, to a certain extent the sodium thiosulphate from diffusing too rapidly into the paper support.

The use of sparingly soluble thiosulphates,[54] for example alkaline earth metal thiosulphates,[57] instead of sodium thiosulphate in order to reduce the tendency to diffuse has not proved satisfactory. There were serious disadvantages: for example it lengthened the time of contact or reduced the density of the positive image.

In order to prevent premature decomposition of the thiosulphate in the layer during storage the pH of positive layers containing sodium thiosulphate is adjusted to at least 5–6. Moreover, when the sodium thiosulphate is incorporated in the positive layer its optimum concentration should be accurately

* In the case of old positives which have been stored in moist conditions, the sodium thiosulphate which has diffused into the paper can easily be detected by making a spot test on the back of the positive with a silver nitrate solution containing acetic acid. This reaction produces a yellow stain consisting of silver sulphide, the intensity of which gives at the same time a direct measure of the quantity of sodium thiosulphate present in the paper.

maintained. In fact, too high a concentration of sodium thiosulphate gives rise to the formation of stable thiosulphate complexes with a low silver content, and these complexes are difficult to reduce or cannot be reduced at all, particularly when the redox potential of the developer has decreased, either by a decrease in pH or by reduction of the developer concentration. The optimum amount of sodium thiosulphate in the positive largely depends on the quantity of silver supplied by the negative, on the activity of the developer and of the nuclei as well as on the swelling properties and absorptivity of the positive. This concentration generally lies between 1 and 3 g of sodium thiosulphate-5-water per sq m. A real disadvantage of this system is the increase which takes place in concentration of thiosulphate in the developing liquid, when the latter has been used repeatedly. This brings about a reduction in image density, on the one hand by solution of the silver salts from the negative, which are thus lost to the transfer process, and on the other hand by the formation of stable silver thiosulphate complexes which are no longer capable of being reduced.

Examples of positive materials which do not contain thiosulphate are Copyrapid-Dry-Positive and Copyrapid-Multi-Positive.[53–7]

The first named material contains an image-receiving layer which is so thin and is of such poor swelling power that the requisite thiosulphate for the adequate transfer of silver cannot be incorporated in it and it must therefore be present in the developing liquid (see 3.4.2).

The multi-positive material, as its name implies, is used for producing more than one copy from one and the same negative. Since the thiosulphate would dissolve the unexposed silver halide too rapidly from the negative, owing to its very high silver complexing constant (see 6.3), the less active sulphite present in the developer or activator solution is used here as a complexing anion to enable the DTR-process to be repeated many times with the same negative (for further details see 3.1).

3.2.2.5 *Other additives present in the positive material.* Compounds which influence the image tone and change it to a neutral black are also added to the image-receiving layer of the positive material. For this purpose, organic mercapto compounds are mainly used.[49,50]

A means of controlling the tone of the image by the addition of nuclei-active substances is essential in the case of the positive since there are many factors which may cause the image tone to turn red-brown or yellow-brown in colour. When the grains of the silver deposit are too small, even though they may give a very dense coverage, brown images are formed. Too high a concentration of nuclei in the positive also gives rise to brown image tones. On the other hand, such additives can only be added in limited amounts since they either inhibit the deposition of the silver or lower the image density or again produce over-toning which means that the image tone is again changed to yellow-brown or yellow (see 3.2.4).

The positive layers also contain alkali-neutralizing compounds, i.e. compounds which neutralize any excess alkali which may be present in the positive after development and which promote yellowing of the copy (see 3.3.1 and 3.3.2).

In principle, development accelerators such as thiocyanates, guanidines guanazoles, amines or hydrazines,[51] 2-amino-1,3,4-thiadiazole-5-thiol[52] or polyhydroxy-ethers,[53] which increase the activity of the nuclei, can also be added to the positive.

Moreover, the image-receiving layers may also contain optical brightening agents as well as blue or red dye pigments to improve the white areas in the background.

3.2.2.6 *Flatness of the positive material.* The positive material should be thoroughly flat not only before processing, when sheet dispensers are used but also after processing, i.e. when the copy is obtained.

Many factors are involved in obtaining an adequately flat positive before and after processing. Firstly, mention should be made of the paper base itself, the flatness of which greatly depends on the conditions under which it was manufactured in the paper factory. Moreover, the various layers which have been applied to the paper base generally possess widely differing swelling properties which influence the flatness of the positive material. Therefore, the coated layers are always kept as thin as possible. Moreover, both the relative humidity of the surrounding air and the temperature greatly influence the tendency of the positive to curl and it is difficult to obtain positives, which will be flat in all climates, by the use of these positive sheets on a paper base which is coated on one side only.

When the back, or paper base, and the front, or image-receiving layer, of a positive material absorb considerably different amounts of the developing liquid, there is a strong tendency for the material to curl because the two sides of the material take different times to dry. For this reason, some manufacturers apply an anti-curling layer to the back of the positive and this is done for instance in the case of Hishi-Rapid-Material. This anti-curling layer causes the front surface to curl in the opposite direction and thus improves the flatness of the material. This anti-curling layer may also have exactly the same composition and structure as the image-receiving layer on the front surface thus enabling the resulting positive material to be used as a two-sided positive, no special marks being necessary to enable the front surface to be distinguished from the back (e.g. by cutting off a corner or printing on the back). The problem arising from the different times taken by the front and back of the positive to dry is of particular importance because with the most recent developing apparatus available on the market only the negative is moistened with the developing liquid, and the dry positive is pressed into contact with the moist negative between the pressure rollers. It is evident that in this case the positive, after having been separated from the negative, will show a much greater tendency

to curl. To counteract this tendency the image-receiving side is dried much more rapidly than the back. In any case, special measures should be taken in order to obtain flat copies and these measures will depend on the particular kind of positive material which is being used.

3.2.3 NUCLEI. During the chemical development of photographic layers, the silver specks formed during exposure catalyse the reduction of the exposed silver halide grains. The silver halide may also be dissolved, previously leaving only the specks behind in the layer. When such a layer is afterwards treated with a developer containing dissolved silver salts, the specks increase in size and the image becomes visible ("physical development").

The combination: developer solution/silver complex salts is an unstable system, having a tendency to precipitate metallic silver, a reaction which can be drastically accelerated by the use of so-called "nuclei". These can be built-up from finely divided metallic silver particles. Their accelerating action can be explained in analogy with the phenomenon of the crystallization of a supersaturated solution by the addition of a single crystallite. It is this kind of physical development which occurs in the case of the DTR-system, with the nuclei having already been dispersed uniformly in the positive layer during coating. The amount of silver required to build-up the image is supplied by the non-exposed areas of the silver halide negative layer, i.e. the image-wise reproduction of an original on the positive takes place with the help of the negative.

The silver salts in the positive can also be precipitated as silver sulphide, if a sufficiently large amount of a sulphide is added to the layer. In the literature the use of colourless zinc sulphide is recommended.[58] In practice, however, the silver precipitation method is favoured when nuclei are used. Moreover, the tone and density of the positive image can be varied within wide limits by modifying the number, the dimensions and the nature of the nuclei. For the sake of completeness, it must be mentioned that when an aluminium plate is used as the positive (see 4.2.1) the silver is deposited by electrolytic development which is brought about by electron-exchange.

The reduction of the silver salts diffusing into the positive layer must take place rapidly, in order to obtain a sharp image and to permit the transfer of a large part of the silver salts to the positive. When choosing the number, the dimensions and the nature of nuclei the following points have to be observed:

Population density of the nuclei must not exceed a certain maximum otherwise the positive image may be coloured. According to Eggert and Ahrens[59] the speed of reduction of the silver salts is not governed by the weight, but by the surface, i.e. in effect by the number of nuclei. During processing the negative layer also contains nuclei, fog silver and reduced silver halide grains. If e.g. nuclei of approximately the same size as the developed silver grains in the negative were to be added to the positive layer, no image would appear since the number of nuclei would have to be kept small so as not to colour the layer.

Only when the positive layer contains a large number of very small nuclei will the silver be deposited relatively rapidly so that a sufficiently high silver salt gradient is maintained until a large part of the silver salts available has been reduced.

In the negative/positive system, only a limited amount of silver salts is available since their only source is the silver halide in the negative layer. If the dissolved silver salts find only a few nuclei available, the latter will grow rapidly. The resulting positive has a black image-tone, but it also has a rather poor covering power. Otherwise, the nuclei grow slowly and the positives exhibit a brownish image tone, but are homogeneously covered.

If extremely high concentrations of nuclei are used the silver is only deposited in the upper parts of the positive layer. A study of sections under the optical microscope, reveals that only a thin silver strip remains.[60] This extremely high degree of packing of the silver particles which is unobtainable with any other photographic system, sets up new relations between colour and covering power. Such layers exhibit images of very high covering power, and brownish image tones can more easily be avoided. The presence of a large number of nuclei in the positive layer makes it possible to keep the layer very thin. In an extreme case the nuclei are evaporated on to the surface of the positive layer.[61] For a given number of nuclei, the image tone of the positive can then be varied from brown to neutral depending on the quantity of dissolved silver salts available. In the non-exposed areas of the negative, the concentration of the dissolved silver salts is highest whereas the relative concentration of the nuclei in these areas is lowest.

In practice, only the fog silver is present, but this can be suppressed by taking adequate measures.

On the other hand, in the areas of medium-density less silver salt is available, and some of this is deposited in the negative on the surface of the developed silver halide grains which themselves act as nuclei. The result is that neutral black image tones can be obtained more easily in the areas of high density than in those of medium density. This can be illustrated by the following example:

In the case of an office copying material the weight of the nuclei is only 1/1000th that of the silver in the negative layer. As can be proved by control tests, the nuclei are however about 1,000,000 times more active than the reduced silver halide grains in the negative layer owing to their relatively larger surface area.

According to Rott[62] nuclei which give good results in the DTR-positive layer are substantially smaller than the specks which would induce the physical development of the exposed silver halide grains to take place. In electron microscope investigations, magnifications of 20,000 times were insufficient to render the nuclei visible. Only at very high magnifications (about 300,000 times) were the scientists of Agfa-Gevaert NV able to derive a mean diameter of about 45Å for silver sulphide and nickel sulphide nuclei. Plate 3.2 shows an electron-micrograph of this kind.

(For further details regarding nuclei and the relation between grain-size and image-tone, see chapter 6).

(For the role of certain additions and of the binder in relation to image tone, see 3.2.4).

A very great deal has been written about the chemical nature of the nuclei and their methods of preparation: most of this very voluminous literature consists of patents.

The following compounds are recommended:

1. Metals, such as silver, gold and rhodium. The use of exposed silver halide, reduced to silver during development, is also recommended.[63,64,65]
2. The sulphides, selenides, tellurides, polysulphides, polyselenides of a number of metals, chiefly silver. Moreover, zinc, chromium, gallium, iron, cadmium, cobalt, nickel, manganese, lead, antimony, bismuth, cerium, arsenic, copper, rhodium, palladium, platinum, lanthanum, titanium are mentioned. A mixture of different metal sulphides is also proposed.[58,63,66–73]
3. Easily reducible silver salts form silver nuclei during processing (silver nitrate or silver citrate).[74]
4. Inorganic salts, which react with the incoming diffusing silver salts, to form nuclei. Thus the addition of sodium sulphide leads to the formation of silver sulphide nuclei, whereas the addition of tin chloride leads to the formation of silver nuclei.[75,76]
5. Organic compounds, which contain a labile sulphur atom and which therefore lead to the formation of sulphide nuclei during processing. The following compounds have been mentioned: mercaptans, xanthates, thioacetamide, dithiooxamide, dithiobiurate.[77,78] Organic reducing agents, such as hydrazine derivates or silanes give rise to silver nuclei when evaporated on to silicic acids or barium sulphate.[79,80]

The chemical nature of the nuclei, however, is only one of the factors which determine their activity. The same chemical compound can bring about a large variety of changes in the properties of the material. Thus it is possible to change the dimensions of the nuclei[81] by varying the conditions during manufacture. Here the nature of the protective colloid and the conditions of precipitation temperature, concentration during precipitation, presence of other substances, etc. play an important role.

As far as the manufacture of nuclei hydrosols is concerned there is a very extensive literature on the subject of colloids. Here it suffices to mention the well-known work of Carey Lea[82] on the manufacture of silver sols containing particles of different sizes. Here again gelatin is the most suitable protective colloid for the manufacture of sulphide nuclei. Apart from other binders, organic sols are also recommended[68] (for the influence of the binder see also 3.2.4). If the nuclei are precipitated on to silica gel which has no protective

colloid properties, and the layers are then processed, silver agglomerates are formed: these agglomerates, because of their large dimensions, give rise to black image tones.[66,83,84,85] The substances containing nuclei exhibit a tendency to absorb selectively additional compounds which are incorporated in the layers for the purpose of regulating the image tones. Thus silver sulphide, e.g. adsorbs 1-phenyl-1H-tetrazole-5-thiol better than does nickel sulphide. The speed with which silver is deposited in the positive is therefore retarded less with nickel sulphide nuclei than with silver sulphide nuclei, if both the layers contain 1-phenyl-1H-tetrazole-5-thiol as blue toner (see also 3.2.4). For further details regarding additions, see the literature.[73,78,86]

Polythioethers increase the activity of nuclei which consist of colloidal heavy metal sulphides and metal sulphides and may therefore replace these nuclei either partially or completely. They are able to accelerate the formation of the positive image.[87,88]

The following paragraph gives the procedure for the manufacture of nuclei.[89]

"The nuclei are prepared by rapidly mixing a dilute solution of Na_2S with a dilute solution of one or more metal salts, for example zinc nitrate, lead acetate and $AgNO_3$ in the presence of a critical amount of colloid stabilizer. The colloid stabilizer may originally be present in either the sulphide solution or the metal salt solution, depending on the nature of the particular stabilizer. In some cases it may be necessary to adjust the acidity or alkalinity of either the sulphide solution or the metal salt solution prior to the precipitation of the colloidal metal sulphide particles, to ensure that the stabilizer will be in a properly active state to control the size of the sulphide particles."

In practice, the stability of the nuclei is a property of the utmost importance. Therefore, the use of metal sulphides is generally recommended because they are resistant to chemical attack. Colloidal metallic silver is oxidized comparatively readily, especially in the presence of compounds such as thiosulphates or sulphites. These compounds form stable complexes with silver. Extremely stable nuclei are obtained when silver or certain metal sulphides are treated with ionic compounds of noble metals, e.g. palladium.[67] Also the mixing of a silver salt with sulphides or selenides of other metals such as iodine silver or nickel sulphide was proposed to improve the stability of the nuclei.[90] As already mentioned above, nuclei consisting of gold, mercury, silver or copper and their sulphides and selenides, can be evaporated onto positive layers, which are coated with films of, e.g., sodium carboxymethylcellulose.[61]

If the nuclei are directly precipitated in the paper stock during the manufacture of the latter, no separate nuclei layer is required.[91,92]

For the sake of completeness, it must be mentioned that it is also possible to add the nuclei to the processing solution (see 2.2).[93,94,95,96]

3.2.4 IMAGE TONE OF THE SILVER IN THE POSITIVE. The dependence of the colour of photographic images on grain size and grain structure is connected with the

scattering of light by the silver grains. The grains are formed by the growth of the nuclei as a result of physical development during processing and therefore the colour of the image must, at least at an intermediate stage, pass through the yellow image tones, which are characteristic of silver grains in a state of colloidal dispersion. In the DTR-process, the colour of silver in the positive image may vary from yellow to grey and when no suitable precautions are taken the image tone usually varies from brownish-red to brown.

From the many experiments which have been carried out the following factors were found to influence image tone:

1. The properties, the number and the concentration of the development nuclei in the positive layer (see 3.2.3).[97]
2. The time for which the positive and negative remain in contact (see 3.2.2).
3. The nature of the binding agent in the positive layer (see 3.2.2).[98]
4. The quantity of complexing agent present (see 3.2.2).
5. The presence of additives which influence the image-tone.

3.2.4.1 *Survey of the research carried out on the action of compounds which influence the image tone in the DTR process.* Weyde[99,100] has observed that substances which form sparingly soluble silver compounds, particularly those which are sparingly soluble in thiosulphate, retard the deposition of silver in the positive. As a result, the silver is deposited from more-concentrated solutions in a coarser form, thus giving rise to a black image tone.

Cassiers[98,101,102] has also observed that heterocyclic thiol compounds retard the diffusion and reduction of silver complexes. However, electron-micrographs showed that there were no difference in the size and form between brown and blue image silver.

After intensification of the image by repeated diffusion transfer, the brown silver has a spherical structure whereas the black silver has a hexagonal crystal structure. Electron-microscope observations of ultrathin section of such layers revealed that the amount and size of the silver deposited diminished with the depth of the positive layer, and also that part of the silver deposited protruded from the surface of the layer. Examination by X-ray photography revealed a change in the surface structure of the grains in the black silver which was obtained in the presence of heterocyclic thiol compounds. This change is connected with a greater degree of disturbance in the crystal structure. The change in the nature of the surface of the crystal, gives rise to a neutral image tone owing to reduction in the light scattering.

The black silver image is much more chemically inert than is the brown image silver e.g. to treatment with potassium hexacyanoferrate (III) or potassium permanganate; this is also due to the nature of the crystal surface.

Van Veelen[103] has examined the reduction of the silver thiosulphate complex in solution in the presence of thiol compounds. 1-Phenyl-1H-tetrazole-5-thiol[104] and 1-phenyl-2-imidazolidine-thione inhibit development whereas

6-methyl-perhydro-1,3-thiazine-2-thione[105] slightly activates development. With each of these three compounds black silver is obtained. These compounds are adsorbed to the silver nuclei. By their adsorption, they prevent uniform crystal growth from taking place. They gave rise to the formation of deformed crystals and spherical particles with irregular contours.

By microscope examination of thin sections (800× magnifications) Weyde[97] has found that in the case of brown images the entire layer shows a diffuse yellow coloration with a few isolated black grains, whereas in the case of the black images formed in the presence of, for instance, 1-phenyl-1H-tetrazole-5-thiol, large black particles are uniformly distributed throughout the entire layer. From these observations it could be concluded that through the inhibiting action of the thiol compounds more silver salts are already made available by diffusion in the positive layer when the silver is deposited, and as a result the silver is deposited preferentially from concentrated solutions on a few favoured nuclei. In the case of layers of the same thickness but containing a number of nuclei of several orders of magnitude larger, the silver in the microsection appears only as a continuous thin dark streak. A silver deposit of this kind has a high covering power and makes it easier for changes to take place in the optical qualities of the grain surface, e.g. by the adsorption of certain thiol compounds.

Weyde, Klein and Metz[106] found by electronmicroscope observations of tests carried out with heterocyclic thiol compounds used as blue-toning agents, that the shift in the image tone from brown to deep black was accompanied by only a small enlargement in grain size and that the grain diameter of 1000 Å, which is postulated by the Mie theory for particles ranging from blue to grey in colour is not reached in all cases. However, there were certain areas in which the grains were always found to be more densely packed together when blue toning agents were present than when they were absent. These observations showed moreover that layers with a very high concentration by volume of silver ($>3\%$) possess good covering power and a black image tone. With these high packing densities the size of the particles plays a minor part in determining the tone of the image. On the other hand in layers with a lower concentration by volume of silver and with a grain size not exceeding 0·15 to 0·20μ, the image tone is dependent on grain size. The size of the developed silver increases with increase in the concentration of 1-phenyl-1H-tetrazole-5-thiol, the silver is not distributed uniformly but is deposited in the centre of the layer and the colour tone changes from brown through deep black to grey, whereby the density is reduced. These phenomena are a result of the poisoning of the nuclei which is known to be caused by this thiol compound.[99,107,108,109] In the case of another blue toning agent, viz. 4,4,5-trimethyl-4H-pyrazole-3-thiol[110] the silver particles are smaller than in the case of 1-phenyl-1H-tetrazole-5-thiol and the silver is deposited mainly in the upper part of the layer; it has a high density and black image tone (Figure 3.4).

Van Veelen and Brinckman[111,112] have carried out a series of model tests to examine the action of various blue-toning agents, in solution, by physical development of silver sulphide nuclei, and in the DTR-process. The compounds 1-phenyl-2-imidazolidine-thione, 1-phenyl-1H-tetrazole-5-thiol (8) and 6-methyl-perhydro-1,3-thiazine-2-thione (9), which act as blue-toning agents, give silver grain of irregular form. The neutral image-tone is brought about by the different scattering properties of the irregularly formed silver grains. The two first mentioned thiol compounds strongly inhibit the developments by poisoning the

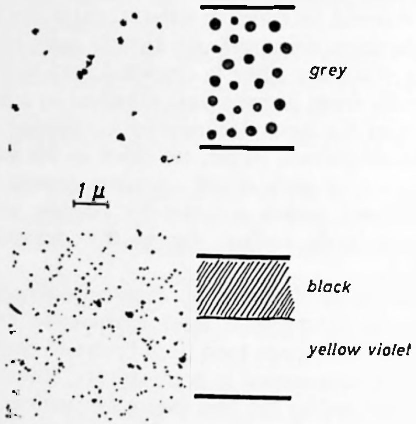


Fig. 3.4. Influence of 1-phenyl-1H-tetrazole-5-thiol and of 4,4,5-trimethyl-4H-pyrazole-3-thiol.

nuclei, and thus cause enlargement of the silver grain. The third compound only slightly inhibits the development, particularly when long times of contact are involved, and hardly changes the grain size (Plate 3.3).

The formation of a neutral black or bluish-black image tone by means of heterocyclic thiol compounds can be ascribed, according to the above-mentioned examinations, to two actions: on the one hand to an enlargement of the silver grain by the poisoning of the nuclei which are thereby reduced in number and on the other hand to a change in the optical properties due to the formation of layers with a higher packing density and with a modified grain surface. For practical purposes, blue-toning agents or combinations of blue-toning agents, the action of which either cannot or can only partly be ascribed to poisoning of the nuclei, are most suitable.

3.2.4.2 *Research on the influence on the image tone of the binding agents in the image-receiving layer.* Cassiers[98] has examined the influence of 12 different

binding agents such as proteins, cellulose esters, polyvinyl compounds and silicic acid on the image tone. In addition to having an influence on the silver deposit, which can be inhibited to a varying degree, the binding agent alters the speed of diffusion. The various binding agents have different degrees of swelling, so that the deposition of silver does not take place at the same concentrations. Cassiers' findings agree with those given in the patent literature,[113] namely that binding agents which do not act as protective colloids for colloidal silver, namely colloids such as silicic acid give neutral image tones, whereas good protective colloids such as gelatin which inhibit the reduction of silver salts give yellow image tones probably by enveloping the development nuclei.

3.2.4.3 *Survey of the patent literature dealing with the influence of the binding agents of the image-receiving layer on image tone, given in the order of sequence of their filing dates*—POLAROID CORP. Binding agents such as silica gel which do not act as protective colloids in relation to the development nuclei, enable silver agglomerates which are black in colour to be formed.[113]

FARBENFABRIKEN BAYER AG. Binding agents, which when used in combination with gelatin, do not result in the formation of transparent layers on drying, for example cellulose derivatives such as methylcellulose, polyvinyl compounds such as polyvinyl acetates, polyvinyl pyrrolidones and other synthetic as well as natural binding agents change the colour of the image silver to black.[114,115]

3.2.4.4 *Survey of the patent lietrature dealing with compounds influencing the image tone*. In the following survey, the patents are listed in alphabetic order of the firms which have filed the patents and in order of the filing dates.

Most compounds, for which tautomeric structures are possible, are given in their thiol form using the IUPAC system of nomenclature. Since many compounds influence the image tone as well as the density, these which only increase the density are also mentioned in the survey. Most of the compounds can be used as an additive both to the image-receiving layer as well as to the developing liquid; a smaller number of compounds can also be incorporated in the light-sensitive layer.

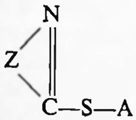
The fundamental compounds mentioned in the patents as well as a typical compound selected from the claims, or examples are enumerated as follows:

AGFA AG (IG-FARBEN AG AND FARBENFABRIKEN BAYER AG). Compounds which form sparingly soluble silver salts in sodium thiosulphate, for example, benzothiazole-2-thiol,[98,116] tetrazole-5-thiol derivatives such as 1-allyl-1H-tetrazole-5-thiol and 1-phenyl-1H-tetrazole-5-thiol,[105] symmetric and asymmetric oxo-dihydro-triazine-thiols such as 4-methylamino-5-methyl-2-oxo-2,5-dihydro-1,3,5-triazine-6-thiol and 4,6-dimethyl-5-oxo-4,5-dihydro-1,2,4-triazine-3-thiol,[117]

perhydropyrimidine-thiones substituted in the 1-position by hydrogen or lower alkyl groups such as 3-methyl-perhydropyrimidine-2-thione[118] and 4H-1,2,4-triazole-3-thiols, preferably substituted in the 4- and 5-positions by lower alkyl groups, such as 4,5-dimethyl-4H-1,2,4-triazole-3-thiol.[119]

FUJI SHASHIN FILM KABUSHKI KAISHA. 1-Phenyl-2-tetrazoline-5-thiones substituted in the 4-position by a substituted aminomethyl group such as 1-phenyl-4-diethylaminomethyl-2-tetrazoline-5-thione,[120] 4-aryl-4H-1,2,4-triazole-3-thiols such as 4-p-tolyl-4H-1,2,4-triazole-3-thiol,[121] 2-1,2,4-triazoline-5-thiones substituted in the 1-position by a substituted aminomethyl group such as 1-morpholinomethyl-4-phenyl-2-1,2,4-triazoline-5-thione[122] and 1,3-thiazoline derivatives substituted in the 3-position by an alkyl group or an aryl group and having a fused cycloalkylene ring such as 3-methyl-4,5,6,7-tetrahydro-2-benzothiazolinethione.[123]

GEVAERT PHOTO-PRODUCTEN NV. The silver image obtained in the image-receiving layer can be toned by means of a selenium or gold bath.[124] In addition, the following blue-toning agents are mentioned: substituted 1,4-dihydro-pyrimidine-2-thiols such as 1-amino-4,4,6-trimethyl-1,4-dihydro-pyrimidine-2-thiol[125] and 1,4-dimethyl-2-mercapto-1,4-dihydro-6-pyrimidinol,[126] substituted 4-imidazolidine-thiones such as 2,2,5,5-tetramethyl-4-imidazolidine-thione,[127] perhydro-1,3-thiazine-2-thione such as 6-methyl-perhydro-1,3-thiazine-2-thione,[105] tetrahydro-2H-1,3-oxazine-2-thiones such as 6-methyl-tetrahydro-2H-1,3-oxazine-2-thione[128] rhodanine derivatives such as 5-benzylidene rhodanine or 5-methyl-rhodanine.[129] Compounds corresponding to the following general formula:



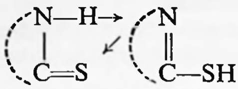
where, Z represents the atoms necessary to close a heterocyclic ring, and A represents a —COR group or a —SO_2R group and R represents an alkyl or aryl group, for example, 1-phenyl-5-acetylthio-1H-tetrazole.[130] 2-Thioxo-1,3-oxazolidine-4-ones such as 5-benzylidene-2-thioxo-1,3-oxazolidine-4-one and 5-methyl-2-thioxo-1,3-oxazolidine-4-one,[131] 3-thioxo-perhydro-1,2,4-triazine-5-ones such as 4,4,6-trimethyl-3-thioxo-perhydro-1,2,4-triazine-5-one[132] and 1,2,3,4-tetrahydro-2-quinazoline-thiones, 2,3-dihydro-4H-1,3-benzoxazine-2-thiones or 1,2-dihydro-4H-3,1-benzoxazine-2-thiones or 2,3-dihydro-4H-1,3-benzothiazine-2-thiones such as 4,4-dimethyl-1,2-dihydro-4H-3,1-benzoxazine-2-thione.[133]

R. GUILLEMINOT, BOESPFLUG AND CO. Tetrazoles substituted in the 1-position by alkyl groups containing from 3 to 14 C-atoms or aralkyl groups containing from 9 to 20 carbon atoms and substituted in the 5-position by sulphur, selenium or tellurium, such as 1-(m-hydroxyethylphenyl)-tetrazole-5-tellurol.[134]

ILFORD LIMITED. Benzotriazoles such as 5-chlorobenzotriazole,[135] 4H-pyrazole-3-thiols substitute in the 4- and 5-positions by alkyl groups or aralkyl groups such as 4,4,5-trimethyl-4H-pyrazole-3-thiol.[110] Replacement for 30 to 50% of the sodium ions of the alkali and the thiosulphate in the developer by potassium ions[136] and the use of 5H-imidazole-4-thiols substituted in 5 position by alkyl or aralkyl groups or in 2 position by alkyl, aryl, alkylthio or arylthio groups such as 2-methylthio-5,5-dimethyl-5H-imidazole-4-thiol[137] have also been mentioned.

KODAK LTD. AND EASTMAN KODAK CORP. 1,3,4-Oxadiazole-2-thiols, 1,3,4-thiadiazole-2-thiols and 2-benzothiazolinethiones such as 5-phenyl-1,3,4-oxadiazole-2-thiol, 5-amino-1,3,4-thiadiazole-2-thiol and 3-methyl-2-benzothiazoline-thione,[138] 2-1,3-oxazoline-2-thiols such as 4-ethyl-2-1,3-oxazoline-2-thiol[139,140] s-triazolo [1,5-a] pyrimidine-7-thiols substituted by thiol groups or substituted thiol groups and by lower alkyl groups such as 2,5-dimethyl-s-triazolo [1,5-a] pyrimidine-7-thiols,[141,142] quaternary ammonium or sulphonium salts the onium group of which is linked to a chain of at least 7-atoms in combination with compounds yielding a silver salt which is less soluble than silver bromide; 42 such compounds are mentioned, for example 1-laury-pyridinium-p-toluene sulphonate, dimethyl-n-nonyl-sulphonium-p-toluene sulphonate,[143] nitroindazole alone or in combination with 3-methyl-benzothiazolium salts such as 5- or 6-nitroindazole,[144] 4-amino-4H-1,2,4-triazole-3-thiol and 1,3,4-thiadiazole-2,5-dithiol,[145] 2-thioxo-perhydro-1,3-thiazine-4-one such as 2-thioxo-6-methyl-perhydro-1,3-thiazine-4-one,[146] 1,2,4-thiadiazole-5-thiols substituted in the 3-position such as 3-methylthio-1,2-4-thiadiazole-5-thiol,[147] substituted 1-alkyl-2-imidazolidine-thione and substituted 1-alkyl-2-thioxo-perhydro-pyrimidinones such as 1-methyl-2-imidazoline-thione, 3-methyl-2-thioxo-perhydro-pyrimidine-4-one,[148] 2-thiohydantoins such as 5,5-dimethyl-2-thiohydantoin,[149] 1,3-thiazolidine-2-thiones and 1,3-oxazolidine-s-thiones substituted in the 3-position by a substituted aminomethyl group such as 3-cyclohexylamino-5-methyl-1,3-oxazolidine-2-thione.[150,151] Mention has also been made of the addition of potassium chloride and trisodium phosphate instead of potassium carbonate to the developing liquid.[152] Thiosemicarbazides or dithiocarbazinates of the following formula: $R—NH—NR_1—CS—R_2$ such as 1-benzyl-thiosemicarbazide, benzoyldithiocarbazic acid methylester,[153] perhydro-1,3,5-triazine-2-thiones substituted in the 1-position by alkyl groups or cycloalkyl groups such as 1-n-butyl-perhydro-1,3,5-triazine-2-thione,[154,159] alkyl-carbonyl derivatives, particularly acetyl

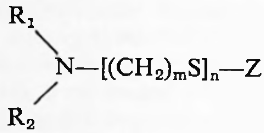
derivatives of compounds corresponding to the following tautomeric structure:



for instance the acetyl derivative of 5-mercapto-3-methylthio-1,2,4-thiadiazole,[155] 4-thiohydantoins such as 5,5-dimethyl-4-thiohydantoin,[156] 1,2,3-benzotriazine-4-thiol,[157] dithia-bis-quaternary ammonium salts of the general formula:

$$Q—R—S—R_1—S—R_2—Q_1$$

where: Q and Q_1 represents a quaternary ammonium salt group or a trialkyl ammonium salt group, respectively R_1 and R_2 each represents an alkylene group and R_1 represents an alkylene group or a bis-methylene-piperazinium group, which are particularly active in combination with thiol compounds: 13 compounds are mentioned such as 7,13-dithianonadecane-1,19-bis-(pyridinium-p-toluene sulphonate),[158] compounds of the general formula:



where: R_1 and R_2 represent a hydrogen atom, a lower alkyl group or an hydroxyalkyl group, m is a low integer, n is 1 to 6, and Z represents a hydrogen atom, HCl, cyanamide- or formaldehyde-groups or a complex-forming metal atom: 12 compounds are mentioned, for example diethylamino-ethanethiol hydrochloride[160] and aliphatic amines containing 14 to 18 carbon atoms such as octadecylamine acetate.[161]

E. N. MASON AND SONS LTD. Combinations of benzotriazole and 3-thiazolidine-2-thione.[162]

OZALID COMPANY LTD. Thioglycolic acid or a soluble thioglycolate such as calcium thioglycolate.[163]

PEERLESS PHOTO PRODUCTS INC. 5-Amino-1,3,4-thiadiazole-2-thiol.[164]

POLAROID CORP. Metal salts and esters in the image-receiving layer which give more stable and more dense images such as the acetates or nitrates of zinc, lead, cadmium and dimethyl oxalate, dimethyl tartrate or dimethyl maleate.[165,166] Benzimidazoles and benzotriazoles such as chloro- and 5-nitrobenzotriazole or 5-methyl- and 6-nitrobenzimidazole,[167] polyethyleneglycol

alkyl thioethers such as polyethylene glycol tertiary dodecylthioethers[168] and cysteine.[169]

3.2.5 THE PROCESSING LIQUID. DTR-materials for office copying are usually developed in an aqueous alkaline solution which, depending on the composition of the negative and positive materials, may also contain silver halide solvents, developing agents, sulphite for the stabilization of the latter, black-toning agents for improving the image tone, and complexing agents for the alkaline earth metals to avoid the formation of the unwanted lime stains which form wherever tap-water is used.

As already mentioned in section 3.2.2, the silver halide solvent—which is almost always sodium thiosulphate—is present in the image-receiving layer of many DTR-positives. A low thiosulphate content of about 1 g/l is suitable for use in fresh, unused, developers in order to improve the processing of Multi-positives which do not contain thiosulphate (see 3.1 and 3.2.2). Larger quantities of sodium thiosulphate (from about 3-5 g/l) however, upset the transfer since in this case some silver thiosulphate complexes of a higher co-ordination number are formed, from which complexes the silver either cannot or else only with difficulty be deposited in the positive by reduction (see chapter 6). This occurs particularly when the pH-value and therefore the redox potential of the developer has been decreased considerably by the uptake of atmospheric CO_2 or by the consumption of alkali by any other means. In this case, only grey copies in which large areas in the black images are inhomogeneous and unsharp are obtained.

In the production of two or more copies from the same negative (double or multi-copies) there is yet another disadvantage for which the abundant supply of thiosulphate is responsible. The silver is transferred so rapidly that insufficient silver is available in the negative for the second, third or fourth copy. From a concentration of sodium thiosulphate of about 5 g/l onwards the preparation of "double" copies becomes impossible.

The developing agents can, in principle, also be incorporated in the transfer layers of the negative and positive materials.[170] (See also section 3.4. Systems using a stable processing liquid.)

All the known rapid photographic developers are suitable for use in the DTR-process. In order to achieve good, rapid and complete development of the negative and the rapid transfer of silver, developers containing hydroquinone and Phenidone are preferable. The great acceleration in development brought about by the superadditive effect of the Phenidone is essential in the DTR-process for achieving complete development of the exposed areas in the negative and therefore for obtaining clear white areas in the corresponding areas of the positive: no other developer combination works more advantageously.

Other developing agents and combinations of developing agents have been proposed, such as polyphenols of the pyrocatechol type, pyrogallol, gallic

acid,[171,172,173] used alone or in combination with pyrrolidone derivatives,[170] further combinations of ascorbic acid and 3-pyrazolidones,[174] etc., but these have not been used as widely as the above combination of hydroquinone and Phenidone.

The alkaline developing liquid has pH of about 11–13, which is adjusted to this value by the addition of the appropriate amount of sodium hydroxide. A great many other compounds which form alkaline solutions in water can be used instead of sodium hydroxide, for example borax, tertiary sodium phosphate, lithium hydroxide, which has been specially recommended for offset developers,[175] or amines, particularly alkanol amines, which have the disadvantage of staining many positive materials and causing them to dry much more slowly since these amines are partly hygroscopic.

The amount of alkali which can be added is limited to the higher pH-value; otherwise the layers or the base undergo a chemical change which is accompanied by a strong yellowing of the copies (see 3.3.1). This amount is also limited to the lower pH-value because the requisite redox potential of the developer is dependent on the pH: at the lowest pH-value, the negative is developed insufficiently and the white areas in the positives are stained by the undeveloped silver salts which have diffused into them.

Potassium ions, when present in high concentrations have an adverse effect on the DTR-process since the potassium silver thiosulphate-complexes formed are rather sparingly soluble. Therefore, the sodium sulphite in the developer cannot be replaced by potassium sulphite which is much more soluble. Ammonia and other organic bases, although they give satisfactory results, are unsuitable for use in practice owing to their very unpleasant smell. Thiocyanates can hardly be used, unless perhaps in combination with thiosulphates. The use of certain substituted ammonium thiosulphates as silver halide solvents has also been proposed.

In order to avoid the formation of brown image tones the developing liquid, just as in the case of the image-receiving layer, can also contain image-toning agents such as heterocyclic mercapto compounds which influence the amount, the nature and the grain size of the deposited image silver (for further details see 3.2.4).

In order to change the image tone to black even when processing is carried out at high temperatures a combination of blue-toning agents and hydrazides such as bisbenzene sulphonyl hydrazide has been found to be very suitable.[176]

The inhibition of development which is often caused by the addition of blue-toners can be eliminated by adding thiocyanates, guanidine and guanazoles.[177] It is also possible to accelerate the development and thus shorten the time of contact by the use of a combination of blue-toning agents and aldehyde and ketone bisulphites.[178]

The formation of unwanted deposits of lime in the positives when tap water is used for preparing or diluting the processing liquid can be prevented by the

addition of complexing agents such as ethylene diamine tetraacetic acid or its sodium salt, or again sodium hexametaphosphate, all of which form complex compounds with alkaline earth metals.

Potassium bromide is used mainly as an anti-fogging agent and is employed in amounts varying from 1 to 3 g/l. It also has a favourable influence on image-tone. However, larger amounts inhibit the transfer of silver and thus reduce the image density.

The silver ions which have arrived in the developing liquid during the DTR-process are reduced when the developer is left standing for a long time, and are deposited in the form of black colloidal silver, which stains the developing apparatus and in certain circumstances even the white background areas in the copies.

In order to limit or even inhibit the formation of silver sludge, the addition to the processing liquid of compounds which combine with the silver ions to form sparingly soluble and non-reducible salts, such as 5, 5-bis-1,2,4-triazole-3-thiones[179] or derivatives of 1,3,4-thiadianole-2-thiols[180] has been proposed.

For the sake of completeness it should be mentioned that the addition of nuclei to the developer has also been proposed (see 2.2).

A basic recipe which can be modified to suit the requirements of the DTR-material and developing apparatus used is as follows:

water	800 ml
anhydrous sodium sulphite	40–80 g
hydroquinone	12–20 g
sodium hydroxide	6–15 g
Phenidone	1–2 g
potassium bromide	1–3 g
sodium ethylene diamine tetraacetate	1–2 g
crystalline sodium thiosulphate	0–15 g
water to make	1 litre

DTR-processing baths are available on the market in the following different forms:

1. as a liquid ready for use,
2. as a concentrated solution which should be diluted before use with the same or double the quantity of tap water, and
3. in the solid state, the organic and inorganic components being in separate packages.

The quantity of processing liquid which is consumed in the production of a DTR office copy of size A-4 is, on an average, about 1–2 ml, depending on the absorptivity of the materials and on the pressure of the rollers in the developing apparatus.

Exhaustion of the processing liquids is caused not only by the consumption of liquid but also by the action of the surrounding air. The uptake of oxygen oxidizes the developer, and the uptake of CO_2 reduces the pH of the liquid. Both effects give rise to copies of reduced image density, which can be improved within very narrow limits by extending the time of contact.

The uptake of oxygen by the developing liquid has the further undesirable side-effect of bringing about a strong coloration of the liquid by the resulting developer oxidation products. The deleterious effect of the action of the air can be counteracted by the use of apparatus with a plastic container (see 3.5) which has been introduced by the manufacturers, whereby the processing liquid is only exposed to the air when it is actually being used.

3.3 *The Photocopy*

3.3.1 BACKGROUND AREAS (WHITE AREAS) IN THE COPIES. For the image quality of the DTR-copies, the white background areas are of at least as great importance as the sharpness, image-tone, depth and uniformity of the black image areas. In fact the image improves with increase in contrast between the black and white areas.

Clear white areas in unprocessed positive material can be obtained relatively simple. Firstly by using strongly bleached paper sheets, which occasionally contain optical brightening agents, as the paper support and secondly, by the addition of blue or red dye pigments as well as optical brightening agents to the white pigment layers (baryta layers) in the positive. A positive does not retain its original whiteness after it has been processed, but turns more or less yellow. A number of factors is responsible for this yellowing, chief of which is the absorption of developing agents by the positive during development.

These developing agents are gradually oxidized by the air, particularly when the positive is stored in humid conditions at higher temperatures, in which case strongly coloured—generally yellow to yellow-brown—oxidation products are formed (quinones, semiquinones as well as their derivatives), a process which is enhanced by the alkaline medium.

Yellowing of the copies is also caused by light, particularly direct sunlight, and is also greatly accelerated by the presence of alkali. Moreover, the coloured oxidation products formed during the development process in the exposed and developed non-image areas of the negative can diffuse into the positive where they colour the white areas. These oxidation products have to be rendered ineffective by the addition of appropriate substances to the positive layer and to the processing liquid.

Finally, a fourth factor which may cause yellowing of the positive should be mentioned, namely the degree of development of the negative. When the negative is not completely developed in the exposed areas, silver salts diffuse into the

white areas, where in the presence of thiosulphate they slowly form silver sulphide which varies in colour from yellow to brown. This silver sulphide yellowing is promoted by the exhausted and therefore comparatively inactive developers as well as by too high a concentration of sodium thiosulphate in the positive or in the developer. In the latter case, silver thiosulphate complexes are formed, such compounds being too stable and having too low a silver content to be reduced (see 6.1, 6.3). They decompose gradually on storage by disproportionation to form silver sulphide.

When no sodium thiosulphate is used as, e.g. in the case of multipositives[181] (see 3.1) and the sulphite in the alkaline developer functions as the sole silver halide solvent, this silver sulphide yellowing does not occur.

Then how can the yellowing of the positive be counteracted?

Depending on the cause of the yellowing, the requisite measures to be taken may differ very greatly.

It has been found that all the measures which are taken to reduce the absorption of liquid by the positive, taking care to maintain the density of the image in the copy, are effective in reducing the yellowing of the positive caused by the uptake of developer. Measures such as diluting the developer, reducing the amount of alkali in the developer, adding salts which greatly reduce the tendency of the layers to swell, or reducing the temperature of development are out of the question. On the other hand, yellowing is reduced considerably by the use of developing apparatus which is provided with a pair of rollers which exert adequate pressure on the materials.

Equally important are the swelling properties of the positive layers as well as the absorptivity of the paper base. On the one hand, the image receiving layers in the positive material should exhibit good swelling properties to enable images free from contact faults to be obtained with the shortest possible times of transfer, and on the other hand the uptake of developer should be kept down to the minimum if yellowing is to be prevented. This problem can be solved, e.g. by means of a baryta layer and this is provided in almost all DTR-positives. This baryta-layer is situated under the actual image-receiving layer and serves to smooth out irregularities in the surface of the paper and at the same time to improve the whiteness of the background in the positive. This layer generally consists of a mixture of barium sulphate, gelatin and occasionally other hydrophilic polymers such as polyvinyl acetate.[182] By the appropriate combination of white pigment and binding agent the swelling tendencies of the baryta layer can be adjusted in such a way that the swelling of the latter is good but takes place more slowly than that of the image-receiving layer. As a result of this, the baryta-layer absorbs the developing liquid down into the layer where the developing agents are not directly exposed to aerial oxidation.

If the baryta-layer were to swell as strongly and as rapidly as the image-receiving layer, the uptake of developer and therefore the degree of yellowing would be increased.

For the same reason, the absorptivity of the paper support is of paramount importance. The absorptivity and the consequent yellowing of the positive decrease with the amount of sizing in the paper base. The yellowing caused by light is also favourably influenced by the quality of the paper base. It is sometimes observed that the yellowing of the positive is not uniform over the entire surface but is heterogeneous, taking the form of small yellow specks and large yellow areas. This is caused by local differences in contact which bring about differences in the uptake of developer. Such faults may be due to too rough a base, an uneven negative layer, heterogeneous swelling of the positive layer, pressure rollers with rough surfaces in the developing apparatus and differences in the swelling or absorption properties of the materials themselves.

It thus appears that the alkali absorbed by the positive during development plays an important part in producing yellowing. Therefore, very many attempts have been made to neutralize the unwanted excess of alkali present in the positive and to render it ineffective.

For instance, one proposal has been to incorporate in the positive layer or in the paper base itself so-called alkali-neutralizing compounds which are compounds with acid properties or are capable of splitting off acids. The nature of these compounds and the amount to be added are dependent on their constitution and mode of action. When the positive layer contains sodium thiosulphate, the alkali-neutralizing compounds should not bring about too great a decrease in the pH-value of the layer since, as is known, sodium thiosulphate decomposes at pH-values below 5. Again, after development, the pH-value of the layer should not become too low since, in an acid medium, the thiosulphate present in the positive would dissolve the image silver and form silver sulphide, which has a disadvantageous influence on the keeping properties of the unrinsed and unfixed copies. As long as the pH-value of the positive layer is sufficiently high, copies with a high sodium thiosulphate content can be kept in an unrinsed and unfixed condition. When the pH-value of the positive layer falls below 5, decomposition of the image silver by the thiosulphate commences and if developer oxidation products (quinones) are also present this could lead to the complete disappearance of the image through the dissolution of the image silver.[183]

Moreover, the alkali-neutralizing compounds incorporated in the positive should not in fact become effective until development has taken place, otherwise the developing process may be restrained or weakened. The requisite conditions can be realized in various ways.

For instance it is possible to choose compounds which split off acid only gradually when acted on by alkali. Alternatively if the acid is split off too rapidly, the compounds can be incorporated in the lower layers of the positive e.g. in the baryta layer or in the paper base itself. The diffusion and saponification of the alkali-neutralizing compounds in the positive should proceed somewhat more slowly than the development. Examples of such compounds, which

are for preference incorporated in the paper base,[184] are acid anhydrides or esters of sparingly water-soluble acids and/or acid salts which form sparingly soluble compounds with water such as acid magnesium sulphate.

In most cases, the alkali-neutralizing compounds are incorporated in the positive layers themselves. Suitable substances are the salts of weak or medium strong bases together with inorganic or organic acids, e.g. triethanolamine-sulphite,[185] sulphite esters of multivalent alcohols[186] such as glycerine sulphite,[199] acetates or nitrates of zinc, cadmium or lead,[187,188,189] alkyl esters of polybasic organic acids such as dimethyl oxylate or dimethyl tartrate[188,190] and other esters, amides or lactones[191] as well as salts of volatile organic, preferably aliphatic, amines.[192,193]

Developing liquids which contain as alkali only volatile amines such as di-or triethanol amine or diisopropylamine can only be used for special DTR-materials[194] and are unsuitable for the processing of normal office DTR, materials because the pH-value of the liquid is too low and other unfavourable side-effects arise such as an increase in the time of drying and staining of the positive layer.

In order to eliminate the yellowing which is due to developer oxidation products, reducing compounds which themselves form colourless oxidation products can be added to the positive. Compounds with molecules containing the tautomeric keto-enediol-grouping —CO—CHOH— or —COH=COH— in a chain or in a ring-system[195] such as ascorbic acid are suitable for this purpose.

After-treatment of the copy with a solution to neutralize the alkali[196,197,198] and reduce the developer oxidation products is not carried out in practice, because of the additional processing stage involved. However when the copy is intended for archival purposes it is advisable to rinse the copy or give it an after-treatment.

In summarizing it can be said that by taking suitable measures, yellowing of the white areas in the copy by light and developing agents, particularly in the presence of alkali and by the formation of silver sulphide, can be prevented.

Note. In the archives of Agfa-Gevaert, copies which are more than 15 years old and which still show no signs of yellowing, even though they were not rinsed after processing are to be found.

3.3.2 THE KEEPING PROPERTIES OF DTR COPIES. The keeping properties of DTR copies depend first and foremost on the quantity of processing chemicals which is left behind in the materials, since the DTR-process is used chiefly in rapid copying processes in which the rinsing step is omitted. In principle, the influence of residual chemicals is already known from experience with conventional photographic papers: here, however, this influence only makes itself felt to a slight extent in the faults which appear in the material when it has

not been very efficiently processed and especially when the processing agents have not been washed out sufficiently thoroughly.[200]

The three chief manifestations of a change in the keeping properties of the copies are:

1. A strong yellowing and browning of the white image area (see 3.3.1).
2. The transformation of the black silver image into a brown silver sulphide image.
3. The bleaching of the silver image, accompanied by the formation of a brownish halo around the former image.

3.3.2.1 *Observation and elucidation of the reactions.* Each of the three changes enumerated above depends in a different way on the storage conditions. When the copies are stored in a cool, dry, store-room, all three reactions are greatly retarded, whereas under the influence of moisture, heat, or both moisture and heat they may undergo various degrees of acceleration.

In dry air, which at the same time is at a relatively high temperature, the degree of yellowing is increased, but the silver image is unaffected and remains unchanged.

When the relative humidity is 80–90% it all depends on the temperature as to whether, instead of the normal black silver image, a thinner, brown, but still easily legible silver sulphide image is obtained, or whether the silver image is strongly bleached leaving only a very thin brownish image which is surrounded by a broad diffusion halo of brownish silver sulphide. Experience shows that at higher temperatures the silver image is transformed into a silver sulphide image, whereas at lower temperatures, e.g. at 22°C, mainly a bleaching reaction takes place.

Bleaching of the silver image and its transformation into a silver sulphide image is probably ascribable to a common initial reaction, viz. to the oxidation of the finely divided image silver by atmospheric oxygen, followed by secondary reactions in which silver ions are formed. Bleaching of the silver image is probably ascribable to this process, since soluble silver salts must be present when the image silver disappears and redeposits around the previous silver image in the form of a diffuse halo. The transformation into a silver sulphide image is also probably due to an oxidation process, since at room temperature, a solid phase reaction between silver and hydrogen sulphide or sulphur is unlikely. Moreover, the presence of moisture is absolutely necessary for the reaction, so that it may be assumed that this process, as well as the bleaching process take place as ionic reactions in a film of moisture which has been absorbed, from the air, to the components of the layer.

The following conceptions can be taken as a starting point for elucidating the processes of the secondary reactions.

At a fairly high temperature (about 60°C), in the first instance a transformation of silver sulphide is observed.

From the time of manufacture onwards the copy now contains relatively large amounts of sodium thiosulphate and sodium sulphite, which in a moist atmosphere at a fairly high temperature and in a weakly acid medium can decompose sufficiently rapidly with the formation of sulphur, hydrogen sulphide and polythionic acids. The resulting amount of hydrogen sulphide is presumably sufficiently large for the immediate transformation on the spot of any silver ions, resulting from oxidation, into silver sulphide. In this way the silver image is replaced by a silver sulphide image which, however, occupies the same position as that of the previous silver image. It is still sufficiently sharp and easily legible. If the temperature drops and the relative humidity remains the same, the rate of decomposition of thiosulphate is likely to slow down. The silver ions formed, now have the opportunity of diffusing away and are not transformed into silver sulphide until later on. For this reason, at room temperature, the change in the image silver is governed largely by the diffusion process. In fact the oxidation of the image silver is also retarded, but it still proceeds at a clearly recognizable rate, whereas the formation of sulphur from the sulphide is probably retarded to a much greater extent.

Therefore the silver ions produced by oxidation have to diffuse through a greater distance. They diffuse away from the site of their origin and not until then are they precipitated in the form of blurred diffusion halation by the sulphide which has been formed in only small amounts.

The fact that the reactions of oxidation and decomposition of thiosulphate with sulphite to form a so-called Wackenroder liquid are not dependent in the same way on the temperature is difficult to prove because a number of separate processes which take place together and successively is involved, the details of which have not yet been elucidated completely.

The pH of the layer also exerts a considerable influence on the stability of the silver images. If the layer is alkaline in reaction, the white areas in the image do in fact become more yellow, but in this case the black areas are stable even in moist conditions of storage and do not fade or become transformed into silver sulphide. If the positive layer is acid in reaction, the process of oxidation proceeds relatively rapidly and the text image will soon fade.

3.3.2.2 *The oxidation reaction.* The reason for the rapid oxidation of the metallic silver, which in other respects and in comparison with other metals is relatively noble and resistant, is based on the hypothesis given above for the reactions of transformation and is arrived at from the following considerations.[201]

The two fundamental equations for the oxidation of silver by oxygen are:

$$4Ag \rightleftharpoons 4Ag^+ + 4e^-$$

$$4e^- + O_2 + 2H_2O \rightleftharpoons 4OH^-$$

For the oxidation potential of the oxygen it follows therefore that:

$$E_{O_2/OH^-} = E^\circ_{O_2/OH^-} + \frac{RT}{2F} \ln \frac{p_{O_2}{}^{\frac{1}{2}}}{[OH^-]^2}$$

When the concentration of hydroxide ions is replaced by the corresponding concentration of hydrogen ions it is found that:

$$E_{O_2/OH^-} = (E^\circ_{O_2/OH^-})^1 + \frac{RT}{2F} \cdot \ln p_{O_2}{}^{\frac{1}{2}} + \frac{RT}{F} \ln [CH^+]$$

By introducing the pH (= $-\log[CH^+]$) one obtains:

$$E_{O_2/OH^-} = (E^\circ_{O_2/OH^-})^1 + \frac{RT}{2F} \ln p_{O_2}{}^{\frac{1}{2}} - \frac{2{\cdot}3RT}{F} \cdot pH$$

Since the pressure of oxygen is assumed to be constant when operating in the air, a constant value of A is found for the term $\frac{RT}{2F} \ln p_{O_2}{}^{\frac{1}{2}}$ and therefore:

$$E_{O_2/OH^-} = (E^\circ_{O_2^-/OH^-})^1 + A - \frac{2{\cdot}3RT}{F} \cdot pH$$

This means that with increase in the pH the oxidation potential E will drop. When the pH is plotted against the potential E_{O_2/OH^-} obtained at different, increasing pH-values, the descending straight line in Figure 3.5 is obtained ($p_{O_2} = 1$ atm. $\rightarrow A = 0$).

For the silver potential the following equation is obtained:

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{RT}{F} \ln [Ag^+]$$

This potential is independent of the pH. If it be assumed that the concentration of free silver ions is of the order of magnitude of 10^{-10}, i.e. a value which has been calculated e.g. for a silver bromide emulsion with a $[Br^-] = 10^{-3}$, then a potential of from +200 to +250 mV is obtained (based on the standard hydrogen electrode). On the basis of Figure 1 it is seen that the difference between the oxidation potential of oxygen and the potential of silver, which gives a measure of the driving force of the reaction, is relatively large at low pH-values, whereas in the alkaline range, it diminishes. On the basis of this conception it is thus possible to explain qualitatively the strong pH-dependence of the silver oxidation and consequently, the change in the DTR-images.

However, it is not only the pH which influences the oxidation of silver but also the concerted action of the hydrogen ion concentration and various salts

which have resulted from processing and which have been left behind in the positive layers. Some investigations indicate that, of the substances present in the alkali developing solution, in particular sodium thiosulphate, but also sodium sulphite and hydroquinone should be considered responsible for the bleaching action. This is explained by means of Figure 3.5.

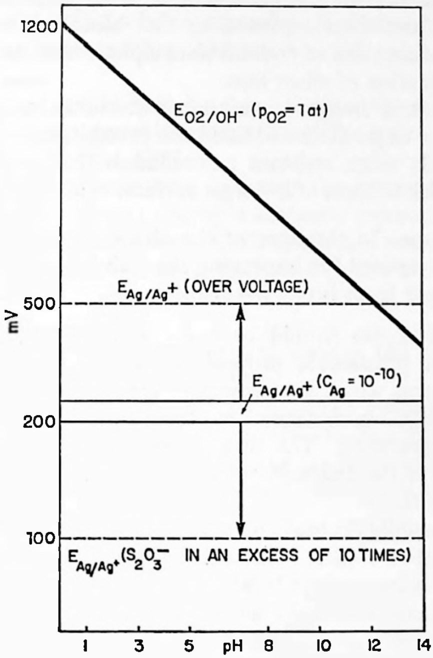


Fig. 3.5. The oxidation reaction.

It should be assumed that oxygen on silver normally possesses an overvoltage of about 250 mV, so that the silver potential is shifted by this amount into the positive range. The potential difference with respect to oxygen is thereby diminished and the oxidation reaction is slowed down. This overvoltage can now be diminished by the oxidation products of hydroquinone, e.g. quinone, so that the potential difference is again increased and the oxidation intensified when products of this kind are present.

However, the main cause of the oxidation reaction might be sought in the presence of the large amounts of sodium thiosulphate which are needed for the diffusion process and which, even after processing, are for the most part, still present in the layer. This brings about a considerable drop in the silver ion

concentration due to the formation of complex ions, and also a large shift in the silver potential into the negative range. Consequently the potential difference, especially in the acid region, increases to such an extent that the oxidation reaction proceeds at a considerable speed.

The complex silver salts which are formed can then diffuse away from the site of oxidation and become precipitated as silver sulphide in a second reaction.

It appears also from these explanations that bleaching is the more intense, the higher the concentration of sodium thiosulphate and, as a result, the lower will be the concentration of silver ions.

Moreover a positive image containing a considerable quantity of silver, which is as compact as possible and had been precipitated with a small surface, will be substantially more resistant to oxidation than a thin and very fine-grained image, which because of its larger surface, will be oxidized more rapidly.

3.3.2.3 *Conclusions.* In the light of the above explanations, what possible means can now be devised for improving the stability of the image and consequently preventing it from becoming bleached?

(1) The finished copies should be made as alkaline as possible. This is, however, hardly a practicable proposition since in the alkaline range the developing substances which are present in the layer are oxidized to strongly coloured compounds, which cause the copies to turn yellow and make them unattractive in appearance. The reverse procedure is adopted: compounds which shift the pH of the finished copies towards the acid region are added (see the previous chapter).

(2) A further possibility is to decrease the concentration of thiosulphate in the layer of the processed copies. This can be done by incorporating the complexing agent, not in the positive layer but in the developing liquid. This procedure avoids any accumulation of thiosulphate in the developer in proportion to the increase in the number of copies, since such an accumulation would intensify the process of oxidation. The finished copies then contain only about one half to one third of the thiosulphate which they would have contained if the salt had been incorporated in the layer. Moreover, the composition of the positive should be such that it absorbs the least possible quantity of liquid and hence of thiosulphate and such that the major part of liquid required for diffusion is supplied by a relatively weak negative, which is capable of swelling.

(3) A further possibility is to change the surface of the silver particles by means of gold or other compounds in such a way as to shift the potential towards more positive values or, in general, to protect the surface from oxidation.[202]

When processing the following points should be carefully noted:

(1) The copies should be produced in a developer which is as fresh as possible thus preventing any increase from taking place in the concentration of sodium

thiosulphate and developer oxidation products in the finished copies, since such compounds are usually present in a developer which has already been used several times. Moreover, in most cases, a higher density is obtained.

(2) The time of contact should be as long as possible to allow as much silver as possible to become precipitated in the positive image, with the result that this silver will be comprised of large particles and have a smaller surface.

(3) The negatives should not be overexposed. If all these measures are taken a denser, more effective silver image will be obtained.

The finished copies should then be dried thoroughly and be stored in an atmosphere of the lowest possible relative humidity which may be permitted to reach, but must not exceed, 60%.

If the copies have to be kept for a long time for information purposes, e.g. for filing in the archives, a short rinsing is advisable especially when storage in dry conditions cannot be guaranteed. If the copies are stored in a more humid atmosphere, they should be kept at as high a temperature as possible, since by so doing a stable residual image of silver sulphide will form sooner and the copies will still be easily legible.

With these conditions of processing and storage the silver images retain their keeping properties for a very long time.

Unrinsed copies have been kept from experiments which were carried out as long ago as 1943. Since the commencement of the manufacture of Copyrapid materials in 1949, copies have been preserved regularly under identical conditions in an office room. These copies are perfectly legible even now.

3.4 *Further trends in the office-copying sector*

A system of making copies should be capable of supplying such copies at any moment and in widely differing circumstances. In this connection a system which employs a developer seems somewhat unreliable because, on the one hand, the developing agents are used up during normal processing and on the other hand these very developing agents are oxidized by atmospheric oxygen, even when the apparatus is not in use. This brings adverse consequences in its train, such as variations in the sensitometric characteristics of the resulting copy, staining of the bath and even of the paper. An attempt was made to reduce the oxidation by atmospheric oxygen to a minimum by passing the processing liquid into a plastic container each time the apparatus had been used and keeping it there at least during the night. This method improves the keeping properties of the bath although however, it is not completely satisfactory. The best system is one in which the developing agents are incorporated in the actual material, thus enabling the processing liquid to be reduced to a mere alkaline solution called an "activator solution". Moreover, the composition of these

materials can be such that they yield dry copies almost immediately in the developing apparatus. As new systems of copying were always being brought out and the demand for dry copies became more widespread, the need arose to develop DTR materials which, while retaining their very high standards of quality, would produce almost dry copies (or copies which became completely dry in a very short time).

A DTR material of this type, under the trade name of "Copyrapid Dry", was placed on the market by Agfa-Gevaert, AG (Figures 3.6, 3.7).

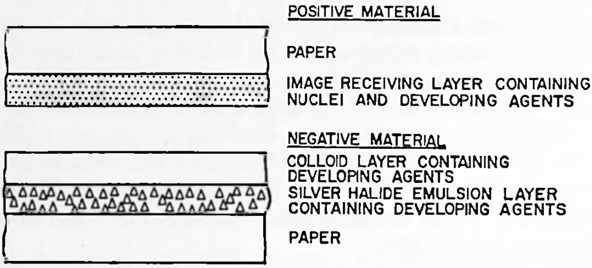


Fig. 3.6. Layer construction of Copyrapid Dry.

EXPOSURE, reflex or by print-through contact

PROCESSING, development and transfer in an alkaline bath (activator solution) containing a high concentration of sodium thiosulphate but no developing agents

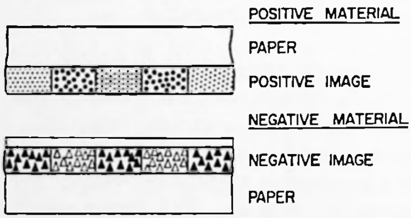
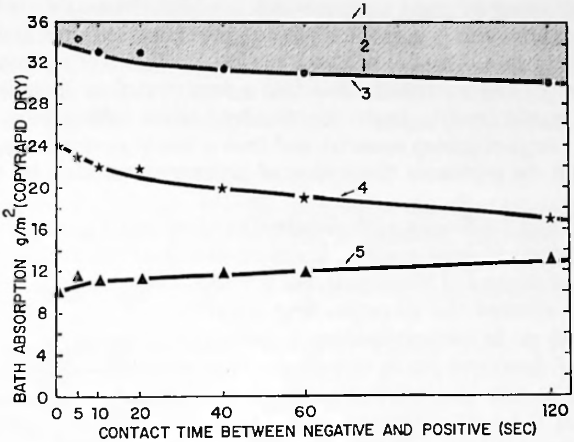


Fig. 3.7. Image formation on Copyrapid Dry.

Remarks:

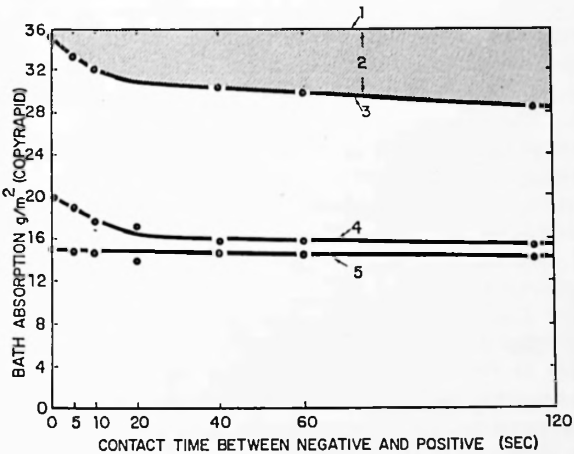
In regard to the negative material, a colloid layer which has good adhering and swelling properties and which does not harden after a certain lapse of time, was applied to the emulsion layer.[203]

In regard to the positive material, the paper support of the image-receiving material should absorb only small amounts of the activator solution, and this is



1. ABSORPTION NEGATIVE AND POSITIVE (THEORETICAL)
2. LOSS BY EVAPORATION
3. ABSORPTION NEGATIVE AND POSITIVE (PRACTICAL)
4. ABSORPTION IN NEGATIVE
5. ABSORPTION IN POSITIVE

Fig. 3.8. Distribution of moisture in Copyrapid Dry process.



1. ABSORPTION NEGATIVE AND POSITIVE (THEORETICAL)
2. LOSS BY EVAPORATION
3. ABSORPTION NEGATIVE AND POSITIVE (PRACTICAL)
4. ABSORPTION IN POSITIVE
5. ABSORPTION IN NEGATIVE

Fig. 3.9. Distribution of moisture in Copyrapid normal process.

made possible either by using a paper which has been thoroughly subbed in the mass, or a paper, which is composed of very fine cellulose fibres and which has been subjected to an intensive post-calendering process (for instance paper of the glassine type) and has thereby acquired a denser surface structure.[204] Such paper bases would tend to make the dissolved silver salts diffuse intensively towards the image-receiving material and thus a sharp positive copy would be produced with the minimum absorption of processing solution by the positive material.

Figures 3.8 and 3.9 illustrate the distribution of moisture in the dry process as compared with the normal process. It can be seen from the figures that, after a normal time of contact of 10 seconds, the dry copy contains only 11 g of activator solution, whereas the corresponding negative contains 22 g of activator solution per sq m. In the conventional processes these values are 17·4 and 15 g respectively of developer per sq m with the same time of contact. Although at first sight the gain in the moisture absorption of the copy cannot be regarded as spectacular (11 g as compared with 17·4 g, i.e. a gain of approximately 30%), it is nevertheless sufficient for considering the resulting copy to be air-dry.

The development nuclei can either be incorporated in the paper itself (in the paper mass of during the sizing of the paper), or be applied to the paper e.g. in a hardened gelatin layer.[205] This gelatine layer may occasionally include a large quantity of white pigments, which even improves the feeling of dryness.

3.4.1 ADDITIONS TO THE MATERIALS. The main developing agent is hydroquinone, the secondary developing agent being 1-phenyl-3-pyrazolidone (trade-name: "Phenidone") or p-(N-monoethyl)-aminophenol sulphate (trade-name: "Metol").

These developing agents can be incorporated in the negative and/or in the positive material during manufacture.[206–10]

A variant is known, in which 1-phenyl-3-pyrazolidone is added to the image-receiving material as the main developing agent, and gallic acid, pyrogallol, gentisic acid, glucose, or furoin is added as the secondary developing agent to the light-sensitive material.[211]

Variants are described, in which the development nuclei are not provided in the material but are supplied by the processing liquid.[212,213] They can be supplied either to the negative material immediately before processing[214] or to the image-receiving material by a special pretreatment in the apparatus.[215]

In all these processes the image-receiving material can either be immersed in, or not be immersed in the processing liquid. In order to obtain still drier copies, it is, for instance, merely sufficient to wet the negative material and subsequently press it into contact with the dry image-receiving material. Apparatus, which have been designed especially for this process, are described in the patent literature[216] and have been sold on a large scale.

In order to prevent yellowing of the dry copy, 3-hydroxy-propylene sulphite[217] can be added to the image-receiving layer.

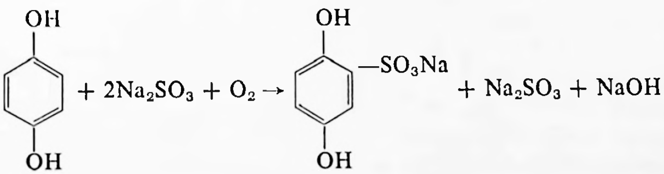
In contradistinction to the commonly used anti-yellowing compounds, which are dispersed in the baryta layer, the above-mentioned compound is soluble in water and consequently is eminently suitable for use in the nuclei-containing receiving layer.

3.4.2 ACTIVATOR SOLUTIONS. For the reducing of the silver thiosulphate complexes on the development nuclei to silver, a minimum pH-value of approximately 10·5 is required. However, the speed of reduction can be increased considerably by increasing the pH-, to values which normally lie between 12·0 and 13·0.

In theory an activator solution is a purely alkaline solution. In practice, however, it contains several components, each of which plays a specific part. For instance the activator solution contains sulphites, which convert the developer-oxidation products into colourless sulphonates. Potassium bromide is added to the activator solution to control the speed of the negative development, whereas sodium thiosulphate is added to make the transfer of the silver salt complexes proceed at the desired rate as in the case of all diffusion transfer reversal processes. Usually, amines and organic mercapto compounds are added to obtain a neutral image tone.

It is not sufficient, however, for the activator solution to have a pH of between 12 and 13 only initially. In fact during development acid is set free. Consequently, it is necessary to keep the requisite pH-value of the layers constant throughout the entire reaction. It follows therefore that in the case of high pH-values, a sufficiently high reserve of alkali must be provided in the activator solution, in other words, the processing liquid should have a sufficient buffer action to absorb the liberated acid without producing too great a decrease in the pH-value. An activator solution with an insufficient buffer action, very rapidly loses the requisite degree of activity and consequently only faint images are produced.

At pH above 11·0 the choice of buffer ingredients is rather restricted. In conventional developers the combination of hydroquinone and sodium hydroxide exerts a favourable buffer action, since, during the oxidation of hydroquinone, alkali is liberated, so that to a certain extent this combination itself brings about the required buffer effect.



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This possibility is of course non-existent in the case of an activator solution, which does not contain any developing agents.

The most suitable buffers for use in the pH-range beyond 11·0 are the phosphate buffers. Potassium salts should not be added to the activator solutions for diffusion transfer systems, because they exert a great influence on the kinetics of the combination of silver ions with thiosulphate to form complex ions. Trisodium phosphate, however, has the disadvantage of forming very voluminous crystals. If part of the liquid evaporates in the apparatus, very voluminous crystal masses are formed on the sides of the apparatus, thus reducing its normal action considerably. This disadvantage can be remedied by the addition of suitable hydrophilic softening agents.

In theory, certain amines, e.g. ethylene diamine and aminoacetic acid can be used as buffer ingredients. These amines, however, give rise to undesirable side effects owing to the formation of silver amine complexes. Thus in general these amines cannot be used as buffers, since these complexes are reduced too rapidly and consequently are not transferred to the receiving layer, and as a result, a lower density is obtained in the positive material.

Amino alcohols, e.g. diethanolamine react in an analogous way. In this case atmospheric oxygen also oxidizes the alcohol group to form an acid group, and this results in a considerable drop in the pH-value of the activator solution.

$$HN(CH_2{-}CH_2{-}OH)_2 + 2O_2 \rightarrow HN(CH_2{-}COOH)_2 + 2H_2O$$

It often happens that silver thiosulphate complexes remain in the liquid and are reduced there to silver. This silver settles down in the form of a sludge at the bottom of the apparatus and is deposited on the sides of the container. Although the risk of such sludge formation is much smaller in the case of activator baths than in a complete developer, organic anti-sludge agents are nevertheless added to activator baths as well. These are mainly products which form more stable silver complexes, for instance silver mercapto compounds, so that the risk of reduction is greatly decreased.

In theory, an activator bath can be used to an unlimited extent on condition that the bath should be replenished by adding the same amount of solution as that which has been removed by the paper. In practice, however, the liquid must be completely renewed from time to time to prevent it from being contaminated by ingredients emanating from the negative and positive materials.

A typical composition is as follows:

water	800 ml
sodium phosphate-12-water	75 g
sodium sulphite	40 g
sodium thiosulphate	10 g
potassium bromide	0,5 g
anti-sludge agent (11)	0,02 g
water to make	1000 ml

The better keeping properties of the activator solution as compared with those of the conventional developing bath used for DTR processes are clearly

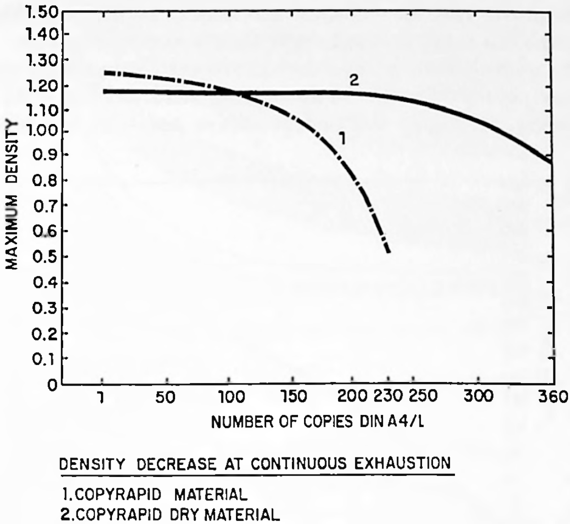


Fig. 3.10. Capacity of activator solutions in dry and conventional processes.

illustrated in Figure 3.10. It appears that when an activator solution is used with dry materials, twice as many copies can be made as can be obtained with conventional processes.

3.4.3 THE RESULTING IMAGE. In general, copies on "dry" material are less black than those obtained by the conventional process. It also appears to be impossible to produce the deep black images which are obtained with conventional DTR processes, even when a known toning agent is used. Elaborate efforts have been made to trace the cause of this phenomenon.

It was not possible to deduce from electron microscopic examinations of the grain structure whether or not this difference in image tone was due to a difference in the specific grain surface of the silver grain (Plates 3.4, 3.5).

Nevertheless, there must be a difference, the existence of which has been proved by the following tests.

Tests were made to compare the reactivity of the silver, which is formed in the two systems. These tests were based on a specific form of DTR development, which was carried out repeatedly on the same surface, each time using a fresh unexposed negative. Measurements proved (Figure 3.11), that the silver formed

by the commonly used DTR process very rapidly displayed a maximum and constant reactivity, whereas the maximum reactivity of the silver formed when an activator bath was used for the dry materials was twice to three times as great. This proves that the surface characteristics of the two kinds of silver differ although this is not revealed under the electron microscope.

It may be assumed that the difference in image tone and reactivity is ascribable exclusively to the differences in the swelling characteristics of the two image-receiving layers, the highly different protective action of the binder on the

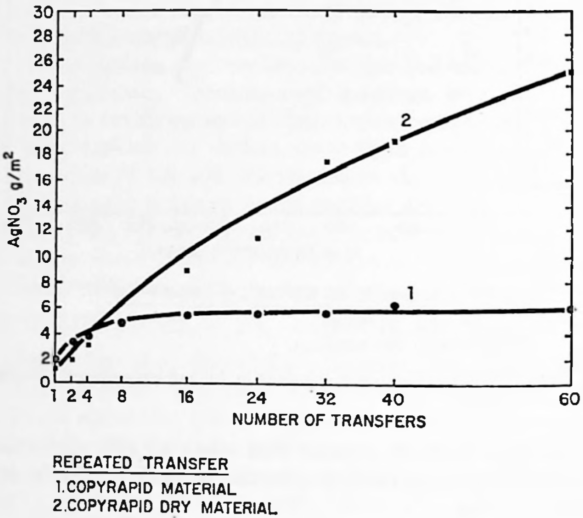


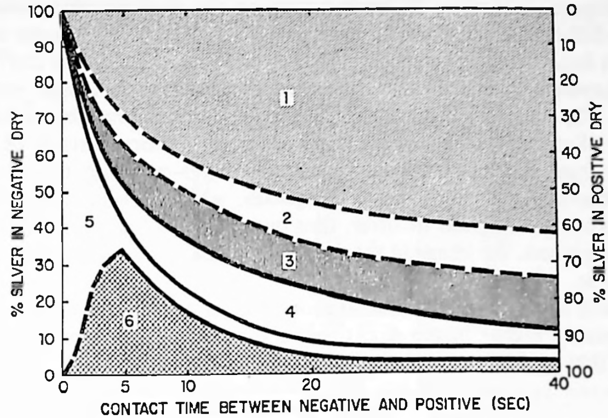
Fig. 3.11. Comparative reactivity of silver formed in dry and conventional processes.

colloidal image silver necessarily playing an important part. This was in fact illustrated by the curves showing the relation between the absorption of liquid and the times of contact (Figures 3.8 and 3.9).

Since any alteration in the swelling characteristics also exerts an influence on the kinetics of the process, a comparison was made of the speed of transfer of silver in the dry and in the conventional DTR processes, respectively. With this object in view a study was made of the balance in the distribution of the diffused silver[218] (Figures 3.12 and 3.13).

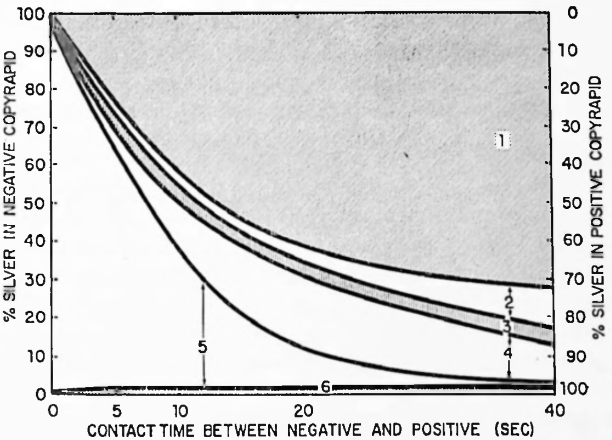
It was found that:

With short periods of contact corresponding with those actually employed in practice, almost identical amounts of silver (expressed as percentages) were transferred in both these processes.



1. SILVER REDUCED IN POSITIVE
2. NON REDUCED SILVER SODIUMTHIOSULPHATE COMPLEXES IN POSITIVE
3. SOLUBLE SILVER SODIUMTHIOSULPHATE COMPLEXES + SILVER LOST IN THE PROCESSING SOLUTION
4. SILVER SODIUMTHIOSULPHATE COMPLEXES IN NEGATIVE
5. SILVER HALIDE
6. FOG

Fig. 3.12. Distribution of diffused silver in dry process.



1. REDUCED SILVER IN POSITIVE
2. NON REDUCED SILVER SODIUMTHIOSULPHATE COMPLEXES IN POSITIVE
3. SOLUBLE SILVER SODIUMTHIOSULPHATE COMPLEXES + SILVER LOST IN THE PROCESSING SOLUTION
4. SILVER SODIUMTHIOSULPHATE COMPLEXES IN NEGATIVE
5. SILVER HALIDE
6. FOG

Fig. 3.13. Distribution of diffused silver in normal process.

The proportion of silver distributed between the photographic material and the bath differs to some extent in both processes. In the dry-process considerably more fog is produced with short periods of contact than in the conventional DTR processes. However this difference decreases with longer periods of contact. The colloidal layer in the negative material probably inhibits the diffusion of silver thiosulphate complexes during short periods of contact and thus these complexes do not reach the image-receiving material at the right moment. As a result, those complexes, which cannot diffuse into the positive layer, are reduced to silver, thus giving rise to fog. Since this silver is lost to the process, the image in the positive material is less black than it would otherwise be.

It is worth noting that the concentration of silver salts in the processing liquid is considerably higher in the dry, than in the normal DTR process. This is probably due to the presence of thiosulphate in the activator solution. In the usual process, however, this thiosulphate is generally present in the positive material.

The fact that in the dry-process the diffusing silver complexes are richer in thiosulphate, and are therefore rendered more easily soluble and less reducible also contributes to the diminution in the blackness of the image.

Although the image obtained by the dry-process is less black than the one produced by the normal process, the copy is nevertheless sufficiently legible for all practical purposes.

In comparison with the system which employs a developer, the system which uses an activation bath represents a great stride forward in the provision of a simple, reliable, and stable system of DTR processing.

3.5 *The Economic Aspects of the Diffusion Transfer-Reversal Process*

3.5.1 EVOLUTION OF THE OFFICE COPY BETWEEN 1950 AND 1972. As demonstrated before, the principal application of the diffusion process is to be found in the field of office copying. From 1950 onwards, an ever-increasing number of photocopying facilities have been finding their way into all kinds of offices both in Western Europe and in the United States of America. These developments are part of the broader evolution of the photographic industry, which from the first years after World War II has been subject to a quite rapid and dynamic growth. The annual increase in the sales of photographic material throughout the world was (and still is) about 7 to 10%. But developments in office copying have progressed even more rapidly: in this photographic sector the figure for the annual increase in sales is as high as 20%. An analysis of various markets shows moreover that there are no actual signs of the market having reached saturation point at the present time. It may even be said that for the time being the office copying market is still fully and steadily expanding. The following figures may give some idea of this evolution.

TABLE 3.2

TOTAL OFFICE COPYING MARKET IN MILLIONS OF DOLLARS (COPYING FACILITIES AND CONSUMER MATERIAL THROUGHOUT THE WORLD)

Years	*U.S.A.*	*Europe and the rest of the world*	*The entire world*
1950	7	3	10
1960	200	55	255
61	250	85	335
62	300	100	400
63	350	120	470
64	450	150	600
65	575	190	765
66	700	230	930
67	900	300	1200
1970	1700	550	2250

TABLE 3.3

NUMBER OF COPIES (IN MILLIONS) ANNUALLY FROM 1960 TO 1972

	1960	*1966*	*1970*	*1972*
U.S.A.	5,000	15,400	62,800	87,000
Europe and the rest of the world	1,000	7,600	31,200	43,000
Total	6,000	23,000	94,000	130,000

3.5.2 CAUSES OF THIS RAPID EVOLUTION. It goes without saying that the steady increase in the consumption of photographic copying materials in offices is due first and foremost to the growing need for making copies. To be sure, this need, although latent, existed long before this spectacular revolution in office copying had taken place, but it could only be satisfied to a limited extent because the earlier photocopying systems were not suitable for the purpose as they involved the use of a darkroom, separate developing fixing and rinsing baths and having first to make a negative and then a positive, apart from being slow and quite expensive. It is true that the photostat photocopying cameras were suitable for making runs of copies, but, owing to their bulk and price, they were only suitable for installation in the offices of large companies. Moreover, more often than not, they only produced negative copies, which from the psychological point of view were not very popular.

It is obvious that, as things were at that time, the old routine methods of making office copies had to be used, namely by means of a typewriter or even copying by hand. Whenever many copies or even dozens of copies were required, carbon copies were typed on the typewriter; or hectographic systems, stencil or duplicating machines were employed. For making one or only a few copies of an original, such systems and machines were not economical.

The quality of the copies was also often unsatisfactory. Thus the latent need for a suitable copying method remained unsatisfied for years. A rapid, easy and cheap system for making good copies was required. Thus looking back on the past, the rapidity with which diffusion copying system was adopted in offices is readily understandable since it satisfied the requirements of the potential buyer. The success of this system became widespread when the diffusion-copying method was perfected and later further developed to enable various types of copy to be made (thin, thick, transparent copies, also recto-verso copies, etc.) and again multiple copies (a number of positives from a single negative). It can be said that the diffusion-transfer copying method has made the modern worker "copy-minded". The ease with which copies could be made available justified its introduction on a broader scale into business and factory organizations. Whereas in the past the office copy had been used almost exclusively as a "document" it now acquired another and more important role: it provided a speedier and better flow of information both inside and outside the company. In this way, not only was the latent need for personally owned "document copies" of letters and memoranda met, but the method became increasingly employed for copies of reports, minutes of proceedings, articles in magazines and daily papers, pages from books and other kinds of printed matter, for transmitting information both inside and outside the company. The office copy gradually became an indispensable element in administrative work and organization. For many years it had been impossible to conceive a modern office without a typewriter. Nowadays a well-organized office without a copying machine to supplement the typewriter is equally inconceivable.

During the years 1950–60 the diffusion-transfer system has greatly promoted the break-through of office copying into business life. There is no need to prove that the systems which appeared on the market at a later stage, e.g. xerography and electrophotography have also turned it to account. This will be made clear below.

To sum up it can be said that the success of the diffusion-transfer method as compared with earlier photocopying method is ascribable to:

(*a*) simplification of image formation (transfer by diffusion)
(*b*) partial automation of exposure and development (appliances with rotary exposure and rotary development) thus eliminating all the intermediate operations and avoiding loss of time
(*c*) the fact that the copy is almost dry on emerging from the developing apparatus and is suitable for immediate use
(*d*) the possibility of being able to make various kinds of copies.

Not only have these advantages satisfied the latent need for making copies, but they have also contributed to the creation of new demands in this field.

The satisfaction of these new demands has also resulted in the extensive and

steady development of this particular market. But at the same time the demand is focused on copying systems of greater simplicity, speed and ease of operation, but at the same time with the price kept down to an economic level. These requirements are specified in Figure 3.14.

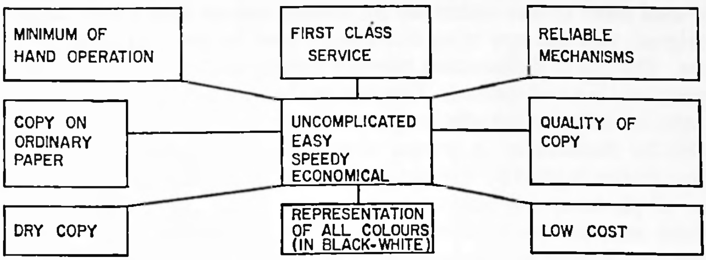


Fig. 3.14. Requirements of modern copying system.

3.5.3 SHARES OF THE VARIOUS COPYING SYSTEMS IN THE RECENT REVOLUTION IN OFFICE COPYING. During the period covering 1952 to 1961 various copying systems appeared on the market in the United States of America. In 1952, American Photocopy (Apeco) started the diffusion-transfer process. In 1953, Kodak followed with the dye-transfer system "Verifax". In 1955, the 3Ms came on to the market with a thermographic system, viz. "Thermofax". During the following five years (1955–60) no new systems worthy of mention made their appearance and the competition between the three said processes was undoubtedly responsible for many of the advancements made in the development of diffusion-transfer apparatus.

The turning point in these developments was reached in the years 1960–61. It is marked by the appearance of electrophotography. In 1960, Xerox, a firm which was not at all well known at that time, brought out a copying machine, which operated on the basis of an indirect electrophotographic principle: the transfer of the image via a selenium cylinder onto ordinary paper.

The Radio Corporation of America (RCA) followed in 1961 with the Electrofax apparatus, an appliance which transfers the image directly on to zinc oxide paper. Both of these electrophotographic methods have their advantages and disadvantages. The drawback of Xerox lies in its use of an indirect method (by means of a selenium cylinder) for producing the image and this results in a rather complicated machine structure and, naturally, the machine frequently gets out of order: but the fact that ordinary paper can be used is a distinct advantage. With Electrofax, the copying mechanism is basically less complicated, but a special paper with a zinc oxide coating has to be used for making the copies. Nevertheless, notwithstanding the drawbacks and

the high cost of hiring the machines, electrocopying meets a basic requirement on the part of the user: namely convenience.

This is the primary and main reason for the success of these photographic copying machines. Another reason may well be that the machines have brought about a change in copying habits. Whereas, previously, copying devices were used more or less exclusively for making one or only a few copies from an original, they are now being increasingly used for duplicating short runs of copies. The line of demarcation between copying and duplicating is becoming progressively less well-defined. This fact has had an unfavourable influence on the sales of diffusion-transfer machines because the latter are naturally less suitable for duplicating. A general idea of the state of the American photocopying market is given by stating that from 1952 to 1966 more than one million pieces of photocopying equipment were sold in the United States, 800,000 of which were in operation at the end of 1966. 100,000 of these apparatus worked on the basis of the direct electrostatic principle, 200,000 on the xerographic principle and all the others, say 500,000 were non-electrostatic.

The proportion of machines using the diffusion-transfer process which were sold was round about 350,000, 100,000 of which were still in operation in 1966. The following table gives a general idea of the distribution of these machines as a function of the volume of copying (number of copies per apparatus per day). It should be emphasized here that the diffusion-transfer process is, of course, suitable for users who only require a small number of copies. The number of these users is very high indeed and it may well be said that the market shows little signs of having reached its saturation point in this particular field.

In conjunction with Table 3.4, Tables 3.5 and 3.6 provide a means of comparing the total volume of sales (in millions of $) on the American market and on the remaining world markets, during the period 1960 to 1970.

TABLE 3.4

DISTRIBUTION OF DTR MACHINES AS FUNCTION OF VOLUME OF COPYING

Copying volume Number of copies per day	*Number of machines*	*Percentage of total number of machines*	*Sales volume in millions of dollars*	*Percentage of total sales volume*
High (225 and more)	100,000	13	400	57
Medium (45–225)	200,000	25	200	29
Low (less than 40)	500,000	62	100	14

TABLE 3.5

VOLUME OF SALES ON THE OFFICE COPYING MARKET IN THE UNITED STATES OF AMERICA (IN MILLIONS OF DOLLARS)

Year	*D.T.R.*	*Electrostatic processes*	*Other processes*
1960	45	3	150
1961	60	31	160
1962	60	85	155
1963	50	160	140
1964	40	275	130
1965	32	418	125
1966	28	599	116
1967	21	814	110
1968	15	1128	101
1969	10	1344	92
1970	7	1582	81

TABLE 3.6

VOLUME OF SALES ON THE OFFICE COPYING MARKET IN EUROPE AND IN THE REMAINING COUNTRIES OF THE WORLD (IN MILLIONS OF DOLLARS)

Year	*D.T.R.*	*Electrostatic processes*	*Other processes*
1960	52	—	?
1961	63	5	17
1962	72	10	18
1963	77	22	21
1964	75	48	27
1965	72	77	41
1966	66	95	67
1967	66	138	86
1968	60	270	70
1969	55	350	60
1970	50	450	50

Taking 1961 as the year in which the rapid changes in the structure of the market definitely started to take place, it can be seen that at that time, in the United States of America the diffusion-transfer process took about 24% of the market, electrostatic ones about 12% and all the other processes (thermography, dye transfer and diazo) about 64%. Nine years later, in 1970, the pattern of the American market is seen to have undergone a complete change: the diffusion-transfer process took only 0·42%, the electrostatic processes took 94·7% and all the others 4·8%. The total volume of sales of office copying in America during the same period grew from 251 million \$ in 1961 to 1670 million \$ in 1970.

In Europe and in the remaining countries of the world a similar evolution can be observed, but this evolution does not develop as rapidly to the disadvantage of the diffusion-transfer process. In 1961 the diffusion-transfer process still held 75% of the market, the electrostatic processes 5% and all the others 20%. The rates in 1970 are respectively 9·09% (diffusion-transfer), 81·8% (electrostatic) and 9·09% (the remainder). The total volume of sales in countries other than America grew from 85 million $ in 1961 to 550 million $ in 1970.

The tables also show that the total volume of sales on the American office copying market is as much as 3 times the total volume of sales in Europe and in the remaining countries of the world. From 1961 to 1967 this proportion of 3 to 1 remained approximately unchanged. It is also obvious that the diffusion-transfer process is primarily a European enterprise. Notwithstanding the fact that the potential American market is three times as large, the "diffusion-transfer sales volume" in the United States has never been higher than in Europe and in the remaining countries of the world. A decline in the volume of sales later on in Europe is clearly evident, showing also a tendency to slow down. The causes of this may be summarized as follows:

1. The makers of diffusion-transfer devices and materials are Europeans. Stress on the European market is more direct.
2. Diffusion-transfer devices are cheaper than electrostatic ones. Since America is in an economically stronger position than Europe, higher costs have a lesser slowing-up effect on sales.
3. "Convenience" of the electrostatic facilities has a greater appeal to Americans than to Europeans.

3.5.4 ACTUAL EVOLUTION OF THE OFFICE COPYING MARKET IN EUROPE (1966–70). Tables 3.7 and 3.8 show the results of extensive market research and of a

TABLE 3.7

PIECES OF APPARATUS IN USE IN GERMANY, ENGLAND AND FRANCE IN 1966 AND 1970

	Diffusion transfer		*Electrostatic*		*Other processes*	
1966	205,000	48·4%	50,000	11·8%	168,000	39·7%
1970	175,000	39·7%	95,000	21·5%	170,000	38·6%

TABLE 3.8

NUMBER OF COPIES EXPRESSED IN MILLIONS PRODUCED IN GERMANY, ENGLAND AND FRANCE IN 1966 AND 1970

1966	340	12·3%	1,880	68·1%	540	19·5%
1970	270	6%	3,600	81·2%	560	12·6%

forecast based on scientific extrapolation. For convenience in setting out the tables they have been restricted to Germany, England, and France as being the countries which are the main users of office copying systems. For instance in 1966 no fewer than 186,250 copying machines were in operation in Germany (of which 115,000 were diffusion-transfer), 123,700 in the United Kingdom (55,000 diffusion-transfer) and in France 104,000 (35,000 diffusion-transfer).

3.5.4.1 *Germany.* Germany, in conjunction with Belgium, is the birth place of the diffusion-transfer process. At present Germany is the principal manufacturer of DTR apparatus in the world. It exports DTR apparatus to all European and overseas countries. For instance, in 1965 the eight German manufacturers of DTR apparatus sold about 20,000 pieces of equipment on their home market and exported about 28,000. It is estimated that 120,000 pieces of DTR apparatus in Germany produce over 200 million copies annually, i.e. an average of 1,600 copies per apparatus. The Agfa-Gevaert Group at present supplies nearly 100% of the DTR paper consumed.

It is obvious that the DTR system will hold its ground for a longer time in Germany than in other countries, for the simple reason that the home market shows a typical structure in that for the most part it is focused on the usage of the DTR system. Moreover, in Germany—a country in which a high standard of quality is the rule—the high quality of the DTR copies also plays an important part: but it is this very quality which is slowing down the inevitable decline of the DTR system. A second cause of this slowing down was the appearance of the "dry" DTR copy in 1967.

3.5.4.2 *United Kingdom.* In contrast to the situation in Germany, there are no manufacturers of DTR apparatus of any significance in England. Moreover, the United Kingdom is the home market of the Rank-Xerox Company in London. Nevertheless, the DTR system, until to-day, has retained a very high share of the market.

In 1965 about 60,000 pieces of DTR apparatus were thought to be in operation. These produced 100,000,000 copies, an average of more than 1,600 copies per apparatus.

The evolution of the office copying market in the United Kingdom enables the forecast to be made that the decline in the DTR system in the U.K. will be a little less slow than in Germany. The draw-backs which make themselves felt in Germany do not exist in the English market.

3.5.4.3 *France.* The position of the DTR system in the French market is not as strong as it is in the German and English markets. There is only one DTR apparatus manufacturer in France. The principal dealers in imported appliances were Sertic, Grog and Photorapid, three firms which in 1968 became part of the Agfa-Gevaert Group of companies. It may be stated that between them

these three firms shared about 65 to 70% of the sales of DTR apparatus on the French market.

In 1965, 36,000 pieces of DTR apparatus were in operation on the French market. 60 million DTR copies were made during that year, an average of more than 1,700 copies per apparatus. As far as it can be seen the decline in the DTR market in France also seems liable to show a more rapid trend than in Germany, although the entry of the firms Sertic, Grog and Photorapid into the powerful Agfa-Gevaert Group may well result in a slowing down in this inevitable decline.

3.5.5 FURTHER OUTLOOK. From the above statements on the evolution of the office copying market, one might be inclined to draw the conclusion that the DTR system had finally seen its best days. This however would only be jumping to conclusions. All the statistics given here refer to the U.S.A. and the principal countries in Western Europe. In these countries the decline in DTR office copying is a normal phenomenon.

Contrary evidence is given by the fact that the production of DTR paper by the leading manufacturers, namely the Agfa-Gevaert Group, remained at the same level in 1968 as in previous years, and was thus much higher than anticipated. This evolution, however, appears normal when one takes into consideration the fact that in countries outside North America and Western Europe there is less money in circulation and that technology is less well developed.

In the less well developed and economically less powerful regions, the office copying market still remains a wide fallow field.

It is obvious that the suppliers of the much more expensive electrophotographic copying machines will have more trouble in the latter markets than will the dealers of quite low-priced DTR apparatus. Moreover electrophotographic copying machines are rather complicated in design, therefore requiring a well organized after-sales service. DTR machines are not complicated and, except for cleaning at regular intervals, require little or no servicing. The latter condition also tends to make the use of the DTR copying system more popular in countries in which at present there is rather a scarcity of trained engineers.

A second factor which will probably be able to slow down the decline in the DTR system, is the development of new applications. Much work is being done along these lines particularly in the research laboratories of Agfa-Gevaert. Most of the new applications fall outside the field of office copying as such: they are primarily directed towards duplicating (office offset in limited numbers of copies), reprography and the printing industries. A short general survey of these various new applications is to be found below.

3.5.5.1 *The DTR "One sheet" systems.* This system for making office copies is easier to use and is cheaper than the conventional DTR system because only one sheet of paper is needed for making a copy, whereas two are

needed with the conventional system. This sheet is provided with a special coating in which both the negative and the positive images are formed (cf. chapter 3).

To make one-sheet DTR copies, ordinary pieces of DTR apparatus can be employed. When the contact method is used, the work can only be carried out by making the exposure by transmitted light, which means that one-sided originals only are suitable for copying. In principle, the one-sheet system can also be used for optical copying, e.g. in document copying cameras with reversing optical systems. With cameras of this kind direct positive copies can be made, and this is a great advantage. A DTR developing apparatus may also be incorporated in the same unit as the camera, thus allowing exposure and development to be performed almost automatically in one operation. It is quite possible that there is still room for such a system on the copying market.

3.5.5.2 *The DTR one-sheet-offset system.* This may possibly be regarded as a further modification in the development of the one-sheet system dealt with under 3.5.5.1: the one-sheet copy provided may be used as an offset-printing forme after it has been treated with an etching solution.

The system is designed for optical exposure (using a copying camera with a reversing optical system). The advantages of this are evident: using only one sheet of paper (thus obviating the preparation of an intermediate negative) an offset printing forme can rapidly be made for an office printing machine. This printing forme is suitable for printing a few thousand copies and its price is so low that it already covers the cost of say ten copies. The final goal, however, is to be able to make DTR one-sheet-offset printing formes by means of a fully automatic system which will supply these printing formes ready for printing at the rate of 3 or 4 per minute. A system of this kind is mainly of interest to the (home) printing departments of the more important firms in which a large number of different printing formes has to be produced daily, whereas the numbers of copies are rather small. As a matter of fact this system could be called a duplicating system rather than a printing system. By the way, the boundaries between the two techniques are becoming progressively less distinct.

3.5.5.3 *The DTR paper offset printing forme.* In contrast to the one-sheet-offset-forme considered under the last heading, the subject which is dealt with here is a paper offset printing forme which is produced by the conventional DTR process, say by means of a negative paper and a positive paper. In certain narrow circles the process is called "printing photocopy", which at once pin-points the circles in which these paper offset formes should be used. While one-sheet offset is designed in the first place in relation to the automatic optical system dealt with under 3.5.5.2 and is intended for the larger firms which are able to purchase such a system, the "printing photocopy" is primarily designed for people who have only an ordinary DTR copying apparatus with contact exposure and a small office printing apparatus (for instance a table-top apparatus) at their disposal.

The aim here again is, of course, to provide an offset printing forme as speedily and cheaply as possible. The DTR paper offset printing forme is basically designed for use by those consumers who purchase DTR aluminium offset plates, but more especially for those who wish for a less expensive method of making specifically limited numbers of copies (a few hundred copies).

3.5.5.4 *The Agfa-Gevaert "Copyproof" system.* Special DTR paper and DTR film materials have been supplied for many years in the United States of America, under the trade name of "Professional Proofing System". These materials are not designed for making ordinary office copies but for making printing proofs, intermediate copies and transparencies for overhead projectors.

This special DTR material gives a high contrast and provides proofs with black areas of high density. Thus it is suitable for a number of reprographical and printing applications. The great success which the "Professional Proofing System" has had up to the present on the American market has been responsible for the placing of this special DTR material on the market under the trade name of "Copyproof" by the Agfa-Gevaert group. It is now also marketed in Europe and in other countries in the world. Of all the new DTR materials dealt with here, the "Copyproof" material is possibly of the greatest interest in the technical and commercial fields because the number of its present and potential applications is so large. It is a fact that, in the field of reprography as well as in that of process work, various processes require the preparation of positive intermediate copies. These (line or halftone) copies must then be used as an "intermediate step" (e.g. in the printing industry) or as "second original" for a copying or duplicating process (diazotype, small offset printing, silk screen printing and other applications).

The classical methods for making such an intermediate copy is well known: a (line or halftone) negative is made on film from the original and this negative is then copied onto film or paper in order to obtain the required positive. This involves: exposing twice, developing twice, fixing twice, rinsing twice and drying twice. With the DTR method (on "Copyproof" material) an intermediate copy or a second original of the kind can be made in one tenth of the time and, moreover the material is less expensive.

Again, all kinds of photographic work can be carried out with "Copyproof" material: two negative papers are available (one for contact work and another for optical work), four types of positive material (ordinary paper, glossy paper, clear film and matt film) and three different pieces of developing apparatus which take materials of respectively 38 cm, 53 cm and 76 cm in width. Considering that the photographic quality obtainable with "Copyproof" material for average work is more than satisfactory, it may undoubtedly be presumed that this new method is likely to contribute also to the further distribution of the DTR process in the field of reprography and in the printing industry.

3.5.5.5 *The DTR aluminium offset system.* This system was originally designed for simple office printing work and was originally used almost exclusively for that purpose. Before long however, it appeared that the system had other potentialities if only a means could be found, when developing and transferring the image, of bringing the negative paper into correct register with the aluminium plate.

This has now been achieved. Developing-transfer apparatus have been on the market for some time: they are provided with a feed-in-system which ensures correct registering of the paper and plate, thus eliminating the necessity of having to make corrections in register on the printing machine. With this technical improvement, the DTR aluminium offset system is now also likely to be used for issuing a far larger number of copies than is required in ordinary routine work, e.g. for the printing of local papers and weekly magazines, reprints of books, etc. The growing importance of DTR offset printing is dealt with in a separate chapter (cf. chapter 4).

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IV. OFFSET PRINTING SYSTEMS

4.1 *Introduction*

The general characteristic of DTR-systems is that the positive image obtained consists of finely divided metallic silver. The high chemical reactivity of this image material on the one hand and the easy and rapid formation of the positive on the other hand made it a very attractive proposition to convert these positives into printing plates for office offset printing. A whole series of materials based on this idea has been developed and successfully placed on the market. They meet the large demand for printing plates which can be prepared rapidly and efficiently without a dark room, and with which hundreds or thousands of copies of an original can be made on office offset machines.

In practice, these systems generally operate in two stages:

the preparation of a positive on a suitable support by the DTR-method;
the chemical after-treatment of this positive for the purpose of increasing the oleophilic properties of the image silver or the hydrophilic properties of the support (or both at the same time).

The vastly increasing interest of consumers in this simple and rapid method of preparing printing masters clearly arises from the fact that office offset systems have been developed from nearly all the variants of the DTR-system.

The following systems are known:

systems using separate negative and positive materials,

with aluminium foil as positive material (4.2.1)
with a paper sheet as positive material (4.2.2 and 4.2.3)

systems using one sheet only,

with the negative layer on top of the positive layer (4.3.1)
with the positive layer on top of the negative layer (4.3.2).

4.2 *Systems using separate negative and positive materials*

4.2.1 ALUMINIUM AS THE POSITIVE MATERIAL

4.2.1.1 *Principle.* A negative material which has been previously exposed is passed together with an aluminium foil through an office copying apparatus containing developer solution. The negative material and the aluminium foil

adhere to each other when leaving the apparatus and after a few seconds are separated. A positive reversal image consisting of metallic silver has formed on the surface of the aluminium plate.

By means of a short after-treatment the resulting bimetallic plate (aluminium foil + silver deposit) is transformed in such a way as to make the aluminium water-receptive and ink-repellent whereas the silver image becomes ink-receptive and water-repellent. An offset printing master is thus obtained.

4.2.1.2 *DTR aluminium offset systems.* The DTR-aluminium offset systems which are available on the market can be broadly grouped into two classes:

(*a*) those in which the aluminium foil—whether or not it has been eloxated—has been previously provided with nuclei. These materials are based on the original DTR-principle

(*b*) those in which the aluminium foil contains no nuclei and which therefore introduce a new principle into the DTR-technique.

According to A. B. Dick (U.S.A.) the image-receiving material for the first process is prepared as follows:

A metal foil (aluminium, zinc or copper) is provided with a soluble salt such as lead acetate after which it is coated with a composition consisting of an alkali metal thiocyanate (e.g. potassium thiocyanate) and a soluble sulphide (e.g. sodium sulphide).[1,2,3]

By means of this treatment developed nuclei are formed.

The following procedure is proposed:

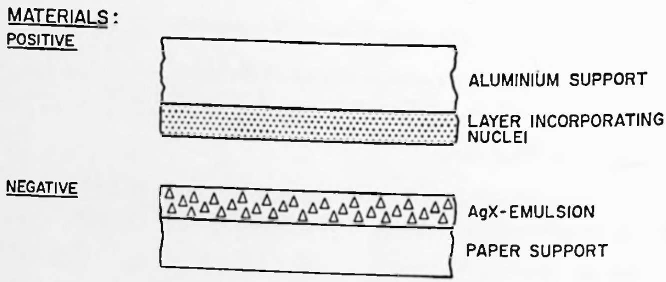


Fig. 4.1. Construction of image-receiving material with metal-foil base.

Exposure: by reflex, contact or optically

Processing: development and transfer using a developer bath containing sodium-thiosulphate in an office copying apparatus

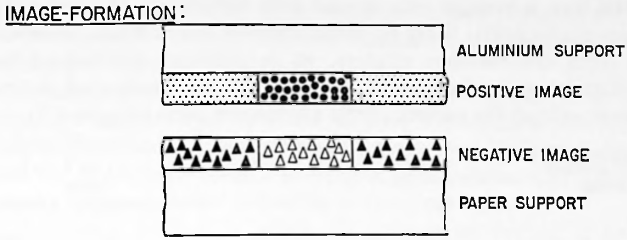


Fig. 4.2. Image formation on aluminium-based material.

After-treatment: (*a*) Rubbing with a lithographic preparation; (*b*) Lacquering.

The printing plate formed in the above-described way is ready for use in office offset printing machines.

The patent literature does not make it quite clear by what action the nuclei—and as a result the image—are made to adhere to the aluminium surface. It is doubtful whether with the procedure described, long runs of printing are achievable.

The Eastman Kodak Company has developed an analogous process which is characterized, however, by the fact that the nuclei are not applied directly to the aluminium surface, but are incorporated in a grained or anodized metal surface (eloxated aluminium), by immersion in an aqueous colloidal dispersion of silver, silver sulphide or gold, free from colloidal binding agent.[4]

In this process the eloxal layer functions as the binder for the nuclei.

It is also possible to incorporate the nuclei in a slightly viscous developer.[5] In this case, the negative contains a colloid layer, which is capable of swelling, on top of the emulsion layer and the aluminium surface need not be given a preliminary treatment.

The negative material used by Eastman Kodak has a waterproof paper support, e.g. paper provided with a polymeric (polyolefin) layer.[6] This has the advantage that more silver is transferred to the printing plate since diffusion to the paper support is inhibited. Moreover, this expedient also promotes the dimensional stability of the material and the negative does not stick to the plate even after long times of contact.

Gevaert-Agfa N.V.[7] has introduced a new image-forming principle into this technique (Copyrapid Aluminium Offset materials). It is based on the observation that in certain circumstances DTR development of a pure aluminium support is possible even in the absence of nuclei. In this case, the transferred silver halide complex is not converted into metallic silver by spontaneous photographic development such as is the case in the other DTR processes but by electrolytic reduction analogous to that which takes place when a solution of

noble metal ions is brought into contact with the surface of a less noble metal (in this case aluminium). Since by this conversion the complex silver ion is also removed from the reaction mixture, as in ordinary DTR-development, a positive silver image is also formed as a result of the diminution in concentration of silver salts at the surface of the aluminium plate (Figure 4.3).

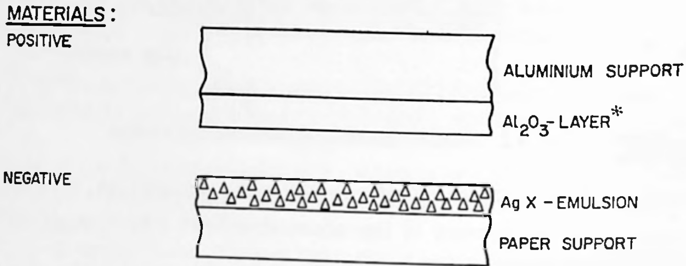


Fig. 4.3. Construction of Copyrapid Aluminium Offset material.

Exposure: by reflex, contact, or optically.

Processing: development and transfer in a (strongly alkaline) developer bath (containing sodium-thiosulphate) using normal office copying apparatus.

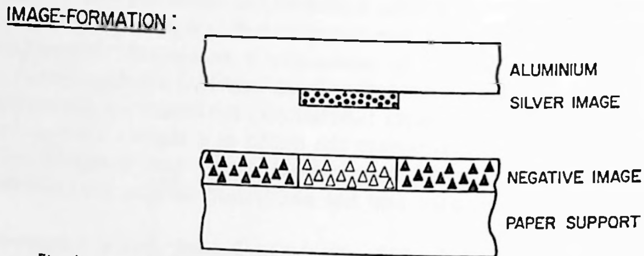


Fig. 4.4. Image formation on Copyrapid Aluminium Offset material.

After-treatment: (*a*) Rubbing with a lithographic preparation; (*b*) lacquering.

4.2.1.3 *Remarks about this process.*

(*a*) Cadmium- or zinc-salts are incorporated in the negative material since it is known from experience that the adherence of the silver image to the aluminium surface is improved thereby.[8]

(*b*) In order to prevent the negative from sticking too firmly to the aluminium plate and also to obtain a denser and more uniform silver image, an

* An aluminium oxide layer forms spontaneously on the surface of the aluminium when the latter is exposed to the air after the manufacturing process. This phenomenon is undesirable in the above process and therefore this layer should disappear through dissolution in the developer during processing before the aluminium plate comes into contact with the negative material. Otherwise, only part of the silver or no silver at all would be reduced.

additional layer consisting of a water-permeable unhardened colloid (e.g. hydroxyalkyl starch or a similar substance) is afterwards coated on top of the photographic emulsion.[9]

(*c*) A calcium sequestering agent (polyaminocarboxylic acid or its salt) is added to the developer in order to bind the calcium salts which are present in the water since it is known from experience that these salts prevent the Al_2O_3-layer from dissolving in the developer and consequently inhibit the electrochemical reduction of the silver salts.

(*d*) An alternative method in which the sodium hydroxide or potassium hydroxide commonly used in the developer is replaced by lithium hydroxide has been described.[11] This reduces the sticking of the negative to the aluminium foil and at the same time largely prevents the bath from becoming exhausted too rapidly. Moreover, the number of plates which can be treated per litre of bath increases.

(*e*) Instead of aluminium foil it is also possible to use a plastic support which is provided with a layer of metal, e.g. of aluminium, by vacuum deposition.[10] A material which is made in this way is less expensive; however, as yet no such material is available on the market.

4.2.1.4 *Conversion of the DTR positive into a printing master* (after-treatment). The positive image obtained forms a bimetallic system consisting of image areas of finely divided metallic silver adhering to a less noble metal support, viz. aluminium. The silver image systems described above, e.g. those which are formed on an eloxal-support can likewise be treated successfully. The purpose of the after-treatment is to intensify as much as possible the oleophilic properties of the metallic silver and the hydrophilic properties of the non-image areas (aluminium support or eloxal-support).

The technique of the after-treatment is very simple. The active substances are supplied in the form of a solution or suspension (usually called a fixer). The fixer is applied to the surface of the plate by slightly rubbing it on with a wad of cotton wool.

From the physico-chemical point of view this after-treatment creates electric charges in such a way that the printing image areas or silver grains become more positively charged (some rendered more oleophilic) and the background areas (the aluminium) become more negatively charged (are rendered more hydrophilic).

In the patent literature various means have been described for intensifying the ink-receptive properties of the silver image. Examples of such methods are:

I. *Organic compounds.*[12,13,14] (*a*) Compounds carrying an oleophilic group such as:

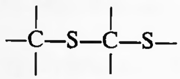
1. mercapto groups

2. SR groups wherein R represents an easily hydrolysable group, e.g. dodecyl mercaptans, benzothiazole-2-thiol, triazinethioles and 1-phenyl-1H-tetrazole-5-thiol
3. thioacid groups
4. thioamide groups
5. the corresponding selenium compounds of these four groups of sulphur compounds.

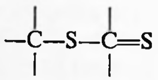
(*b*) Compounds carrying an aliphatic group or substituent of at least 4 carbon atoms, for example, potassium butyl (or octyl) xanthate, s-methyl (or ethyl) isothiouronium which decomposes in an alkaline medium to form methyl (or ethyl) mercaptans.

An example of a suitable fixer composition consists of 1-octyl-1,2,4,5-tetrahydro-S-triazine-5-thiol dissolved in acetone or suspended in a solution of gum arabic.

II. *Cationic surface-active compounds* such as hexadecyl trimethyl ammonium bromide or compounds characterized by a

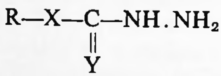


or



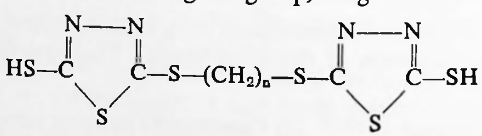
configuration.

III. *Compounds corresponding to the general formula:*



where, R represents an alkyl group containing from 6 to 20 carbon atoms; X represents O, S or NH; Y is O or S.[15]

IV. *A suspension or solution of a* 1,3,4-*thiadiazole-2-thiol* derivative containing at least two mercapto groups and at least two 1,3,4-thiadiazole nuclei which are linked together by means of an organic group,[16] e.g.



(n = an integer)

These compounds can be suspended in alkaline solutions by means of well-defined emulsifiers. They can also be added to the fixer solution.

Another principle which achieves the same end is based on the oxidation of the silver image areas, e.g. by means of cyanoferrates(III) in the presence of metal ions which form insoluble cyanoferrates(II) or cyanoferrates(III).[17]

All these treatments result in the formation of suitable printing plates for use on office offset machines (prints with dense dark image areas on a white background); however, they are only suitable for short-runs of duplicating because during the printing process the printing master shows signs of wear and this results in poor print quality.

Long-runs of printing can be achieved by means of a second after-treatment: lacquers which deposit selectively on the silver image and protect it against early erasure have been found. For this purpose, lacquers based on phenol- or cresol-formaldehyde resins are generally used. Cyclohexanone is used as solvent and linseed oil is used as plasticizer.[18] Instead of a phenol formaldehyde resin an alkyl resin can also be used.[19]

A method in which the fixer and lacquer are combined in one single-treatment solution has also been described.[20] Such a single after-treatment thus enables printing plates suitable for long runs to be produced. The composition used for this treatment consists of organic compounds containing SH—, —NH— or SCN-groups as well as resins, waxes, thickening agents, emulsifiers, and plasticizers. In order to render the silver image more easily visible a basic dye which also deposits selectively on the silver image is added.

After-treatments by means of which image reversal takes place in such a way, that the silver forms the non-printing areas and the aluminium foil the printing area have been proposed. These may be of practical interest in cases in which the originals used are in the form of negatives (e.g. microfilms, printing of printed circuits). For instance, a special after-treatment with a soap solution and a reducer respectively has been described.[21]

4.2.1.5 *Technical literature on the process.* Great efforts have been made to explain the surprising phenomenon of the transfer of silver to aluminium by diffusion without the use of nuclei.[22] At the beginning, the results were inconsistent particularly as regards the anchorage of the silver image to the aluminium support until it was found that images which adhered well to the support were only obtained when the aluminium oxide layer was completely removed during processing and before the aluminium was pressed into contact with the negative.

This finding led to an examination of the behaviour of aluminium in photographic developers and in alkaline liquids. This examination consisted in the quantitative analysis of the amount of hydrogen which was liberated during the chemical attack of the aluminium in baths of different compositions and was carried out using a specially designed Eudiometer (Figure 4.5).[23] From the curves, in which the amount of hydrogen formed per unit area of aluminium surface (H_2 cm 3/m2) is plotted against the time of action of the bath (sec),

the most suitable quality of aluminium can be chosen and valuable information gathered in regard to the composition of the processing baths.

It has thus been found that an aluminium alloy containing certain impurities (magnesium, silicon and manganese) reacts more quickly than does pure aluminium. The same applies to an aluminium surface which has been roughened by brushing: this also reacts more rapidly than a smooth aluminium surface of the same composition. In practice, aluminium having a degree of purity of 99–99·5% is used. If the aluminium has a higher degree of purity,

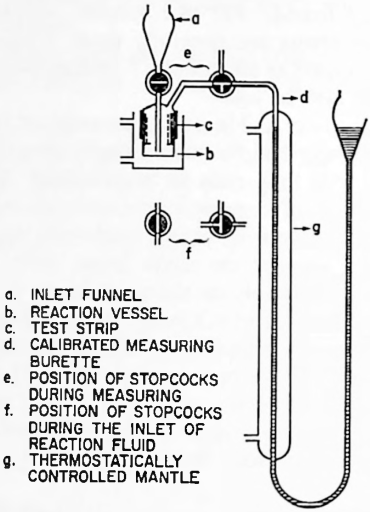


Fig. 4.5. Eudiometer specially constructed for examination of behaviour of aluminium in photographic developers and alkaline liquids.

the Al_2O_3-layer does not dissolve completely and the anchorage of the silver image is impaired.

The above examination has also shown that, when the aluminium oxide layer is attacked by alkali, the alkaline earth metal salts which are always present in tap-water act as inhibitors; metal complexing agents eliminate the inhibiting effect of these alkaline earth metal salts.

It has also been found that by adding sodium thiosulphate to the alkaline etching solution, which is brought into contact with the aluminium, sodium sulphide is formed. However, these sulphide-ions, of which it was first thought that they could act as nuclei, play no prominent part in the transfer of silver to the aluminium.

The principle of this aluminium offset process has been described in detail by the same authors in another article.[23] In this article the formation of the image is explained as follows:

> during the development of the negative, the aluminium oxide layer of the aluminium foil is dissolved in the strongly alkaline developer (pH: 12–13) and, from that moment onwards, the aluminium surface itself acts in the capacity of a reductor for the diffusing complex silver salts.

The electrolytic reduction of these complex silver salts takes place as the result of an exchange of electrons as is the case when a solution of a noble metal salt (potential of silver: +0·8) is brought into contact with the surface of a less noble metal (potential of the aluminium surface: −1·7).

In the process five stages can be distinguished (see also Figure 4.6):

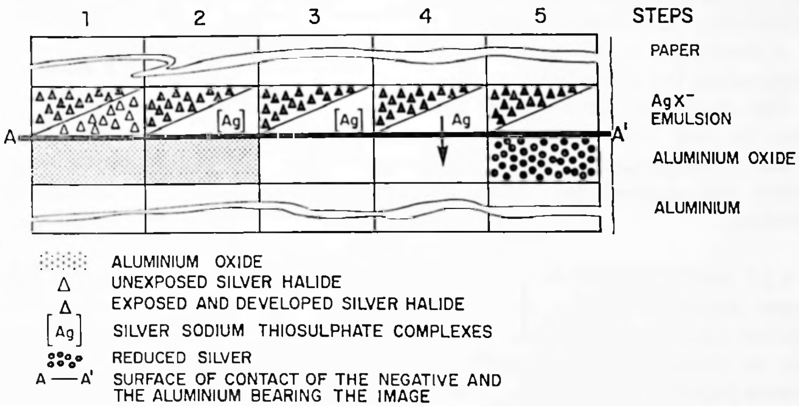


Fig. 4.6. Five stages in the formation of the image in the aluminium offset process.

1. Development of the exposed silver halide
2. Solution of the unexposed silver halide with the formation of complex salts of silver and sodium thiosulphate

$$Ag^+ + S_2O_3^{--} \rightarrow AgS_2O_3^-$$

$$AgS_2O_3^- + S_2O_3^{--} \rightarrow Ag(S_2O_3)_2^{---}$$

3. Chemical reaction between the alkaline developer and the aluminium

oxide layer whereby the latter is removed and the aluminium metal is laid bare:

$$Al_2O_3 + NaOH \rightarrow 2NaAlO_2 + H_2O$$

Stages 1 to 3 occur simultaneously.

4. Diffusion of these silver thiosulphate-complexes to the aluminium.
5. Electrochemical reduction of these complexes by the aluminium:

$$Al^{+++} + Ag(S_2O_3)_2^{---} \rightarrow Ag$$

In the same article it is shown by means of the silver balance that the diffusion transfer process has already come to an end after 10 sec (as compared with the ordinary diffusion transfer process with office copying material described in chapter III where this diffusion transfer process takes at least 60 sec). The authors ascribe this phenomenon to the consumption of alkali by reaction with the aluminium; at a certain minimum pH-value the process stops automatically.

A description is also given of a method of rendering the lithographic effect obtained by the after-treatment visible (see also paper offset).

The aluminium offset process gives good reproduction of up to 120–155 lines per inch, which broadly speaking is adequate for practical purposes.

Run: non-lacquered plates: 2,000 copies; lacquered plates: up to 20,000 copies and even 40,000 copies depending on the quality of the printing machine.

4.2.2 SHEETS OF PAPER AS THE POSITIVE MATERIAL. Offset materials on a paper support, which are considerably cheaper than offset plates on an aluminium support, are also commonly used in offices for offset purposes and can also be obtained photographically. Here again the properties of the DTR-process (rapidity, automatic processing show themselves to their full advantage. However, certain disadvantages which are inherent in paper printing plates (short runs, low dimensional stability) remain.

4.2.2.1 *Processes in which the silver image is the printing element.* Agfa AG describes DTR-processes which are carried out either by means of a tanning processing liquid or by means of a non-tanning processing liquid. In the latter case, however, the image transferred to the gelatin medium should be tanned afterwards, so that in both of these alternative processes a tanned image forms the basis of the lithographic effect. In fact, the tanned image surface is rendered oleophilic and hydrophobic whereas the non-tanned image areas remain oleophobic and hydrophilic. The positive tanned relief image thus formed can be used as a printing master.[24]

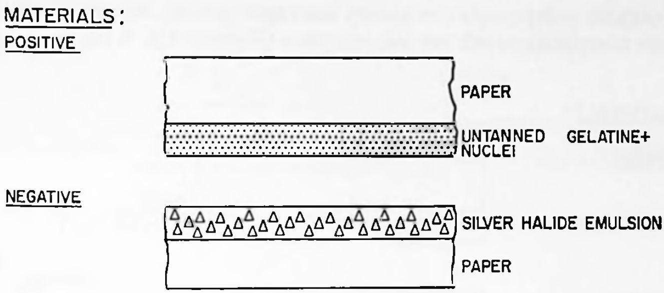


Fig. 4.7. Construction of material to produce tanned relief image.

Exposure: by the reflex or print through contact method.

Processing: development and transfer in an office copying apparatus provided with a tanning developer.

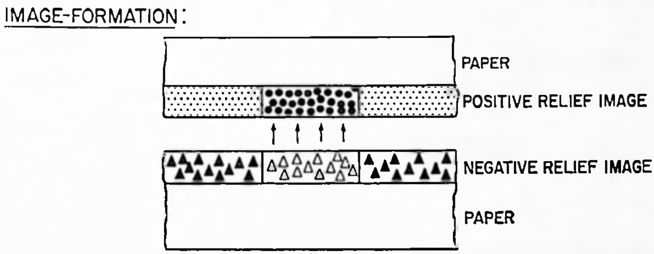


Fig. 4.8. Image formation in material designed to produce tanned relief image.

After-treatment: when a tanning developer is used for the processing liquid there is no after-treatment whereas when no tanning developer is used tanning bleach bath can be employed as in ordinary photography.

Agfa AG has also patented an incomplete DTR-system without DTR-development, which is as follows:

an exposed negative is brought into contact with the receiving material, which is free from nuclei, in the presence of a fixing developer. The silver halide which diffuses into the receiving material is then converted by means

of organic compounds containing mercapto groups into sparingly soluble silver complexes which are ink-receptive (Figures 4.9, 4.10).[25]

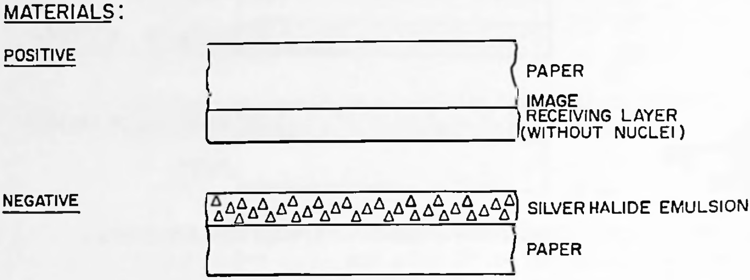


Fig. 4.9. Construction of material for incomplete DTR system.

Exposure: by the reflex or print through contact method.
Processing: in a fixing developer.

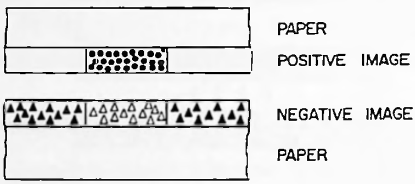


Fig. 4.10. Image formation in material designed for incomplete DTR process.

After-treatment: as described in previous section.

In this process the diffusion is probably incomplete and the amount of silver halide available is small. It is possible for the amount of diffusing silver halide to be sufficient to impart the desired oleophilic properties to the image, but only provided that an after-treatment as described for aluminium offset plates is carried out.

A printing plate has been patented by the firm of A. B. Dick. This plate consists of a metal or paper support, with a hydrophilic surface (consisting of a layer of casein and clay or zinc oxide), nuclei (e.g. tin halide) and a salt of thorium, titanium or zirconium to anchor the oleophilic DTR-image (Figures 4.11, 4.12).[26]

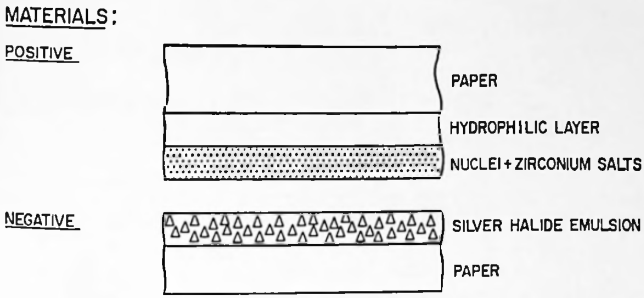


Fig. 4.11. Construction of printing plate by A. B. Dick.

Exposure: by the reflex or print-through contact method.
Processing: DTR-development in an office duplicating machine.

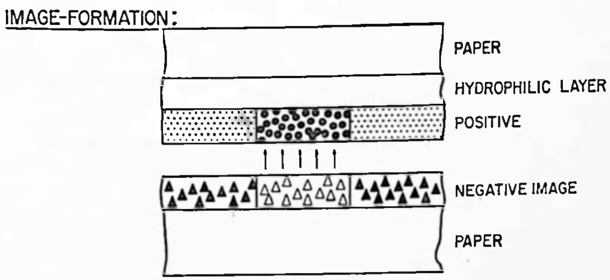


Fig. 4.12. Image formation on A. B. Dick printing plate.

After-treatment: rubbing with a lithographic preparation, as described for aluminium offset plates.

Gevaert-Agfa NV has patented a process[27,28,29] characterized in that the silver transferred has a high density which is used in order subsequently to strengthen the lithographic properties. The positive material consists of a paper support on to which a hardened hydrophilic layer, and on top of the latter a very thin nuclei layer, with a very low content of binding agent as protective colloid, are coated. The developing agents are present in the negative material and an activator solution is used as the processing liquid (Figures 4.13, 4.14).

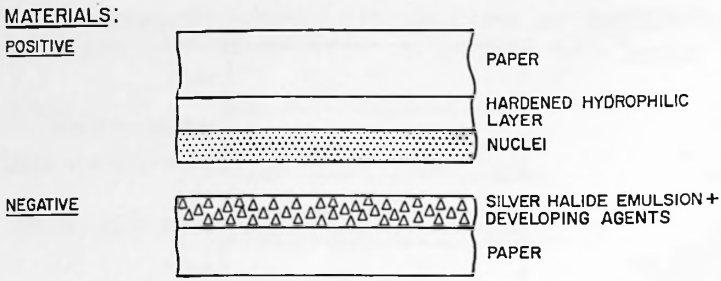


Fig. 4.13. Construction of material for high-density silver transfer.

Exposure: (*a*) by the reflex or print through contact method or (*b*) optically, without a mirror (reduction or enlargement)—in this case the negative material must be of sufficiently high sensitivity.

Processing: DTR-development in an activator solution.

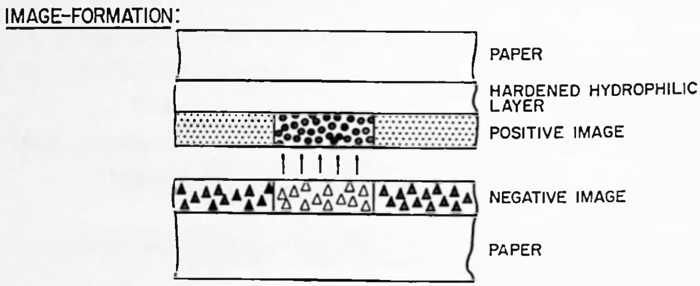


Fig. 4.14. Image formation in high-density silver-transfer material.

After-treatment: rubbing with a lithographic preparation, as described for aluminium offset plates.

Owing to its high density the silver image which is obtained has a metallic gloss and shows great chemical reactivity. This silver image is rendered hydrophobic by a chemical after-treatment and thereby acquires lithographic properties.

The silver can be rendered hydrophobic by different methods which include oxidation by potassium hexacyanoferrate(III) in the presence of metal salts which form insoluble iron(II) or iron(III) cyanide and are precipitated imagewise. A second treatment, for instance with stearylamine, is necessary in order to improve the ink-receptivity.[30]

After oxidation, the silver image can also be converted by means of organic compounds containing SH, SeH, OH or NH-groups, into sparingly soluble complex compounds.[31,32]

These processes require two after-treatments. Therefore, simpler processes have been developed; these include the use of an etch consisting of an aromatic acid (e.g. phthalic acid), a copper salt (e.g. copper(II) chloride) and a silver complexing agent (e.g. potassium thiocyanate).[33] Consequently, one bath serves for the two stages: the tanning bleaching of the silver and the adherence of the hydrophobic substance to the bleached image areas.

Another embodiment which has been proposed is that of adding—in addition to the copper chloride oxidizing agent—certain resins to the same solution.[34]

Another proposal was to subject the silver to an after-treatment with mercury (II) chloride as oxidizing agent which converts the silver into the ionic form,

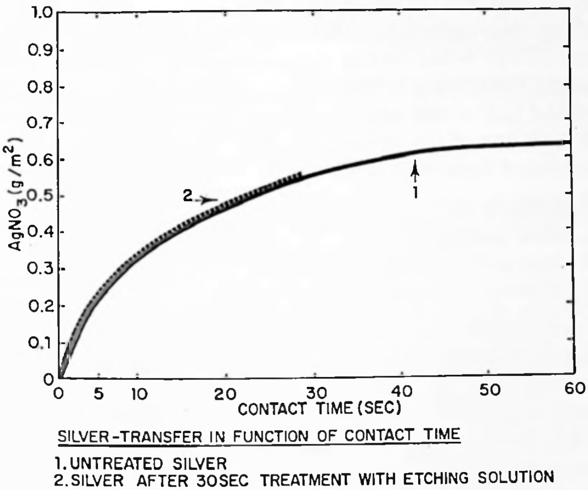


Fig. 4.15. Rate of silver transfer in relation to time of contact with etching solution.

whereby the reduced oxidizing agent combines with the silver salt to form an insoluble complex compound which is immediately receptive to ink, any further treatment being unnecessary.[35]

The mechanism of reaction of all the oxidative after-treatments can be represented as follows:

$$Ag \rightarrow Ag^{+} + e^{-}$$

$$\text{oxidizing agent} + e^{-} \rightarrow \text{reduced oxidizing agent}$$

The reduced oxidizing agent is either itself oleophilic or has a marked affinity for certain oleophilic compounds. The conversion takes place practically quantitatively (see Figure 4.15). An important fact is that in spite of this chemical attack the silver remains firmly anchored to the support: this is obvious from the long runs which are obtained.

One single after-treatment also suffices when potassium hexacyanoferrate (III) is used in the presence of organic compounds which contain a group (a thioxo or mercapto group) which reacts with silver ions.[36]

For this purpose 2-imidazolidine thiones, perhydrooxazine-2-thiones and perhydrothiazine-2-thiones are particularly suitable.

The effect of incorporating the nuclei in a very thin top layer is clearly apparent from the following experiment.

DTR-transfers were carried out on two kinds of positive materials: one in which the nuclei were present in a hydrophilic layer (Plate 4.1) and the other in which the nuclei were present in a very thin top layer (Plate 4.2). In both cases, negatives, one half of which had been exposed whereas the other half remained unexposed were used. The blank background forming the non-printing areas of the offset master corresponded to the exposed half of the negative whereas the silver precipitate forming the printing areas corresponded to the unexposed half of the negative. One half of each of the two plates was then treated with one of the etching solutions described above in such a way that on each plate 4 areas were obtained:

area I: background
area II: silver precipitate
area III: background treated with etch.
area IV: silver precipitate treated with etch.

The four areas in the plate were then partially covered with a lithographic ink: this was done by rubbing the ink across the diameter of the plate in a vertical direction.

It can clearly be seen that the silver image of high density (Plate 4.2) is more receptive to ink than the one which is obtained in the material in which the nuclei and in consequence thereof the image silver is distributed throughout the entire thickness of the positive layer (Plate 4.1).

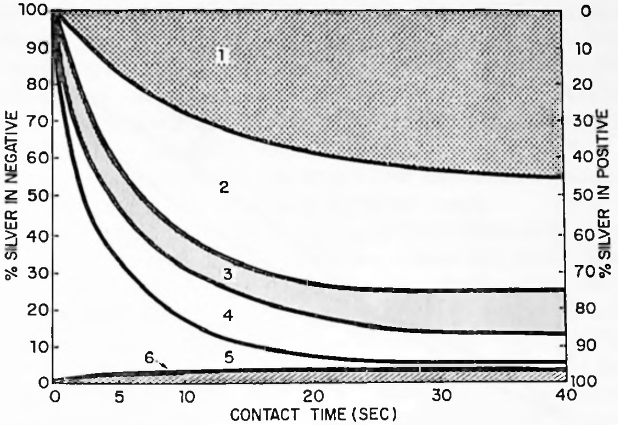
This is confirmed by measurements of the angle of contact.

TABLE 4.1

EXAMINATION OF LITHOGRAPHIC BEHAVIOUR IN DIFFERENT MATERIALS

Areas	*Paper plate*		*Aluminium offset plate**
	Nuclei in layer (A)	*Nuclei on top (B)*	*Without nuclei (C)*
I: Background	28°	34°	15°
II: Silver precipitate	30°	37°	12°
III: Background treated with etch	29°	37°	17°
IV: Silver precipitate treated with etch	28°	69°	30°

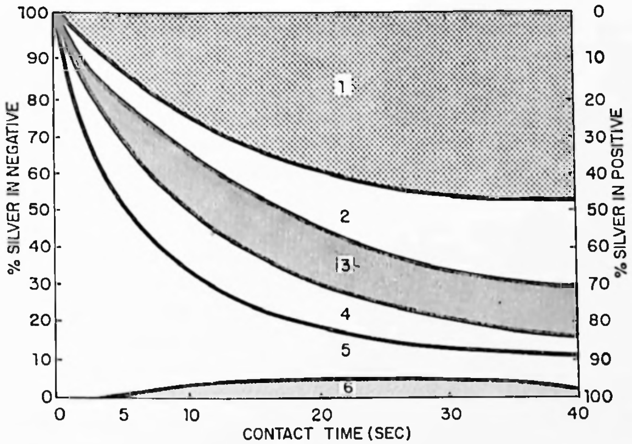
* These results are given for comparison purposes and are mentioned in an article by A. Rott and L. De Haes: J. Photogr. Sci. Vol. 8 (1960), p. 26–31.



SILVER DISTRIBUTION: NUCLEI ON TOP OF THE LAYER

1. SILVER REDUCED IN POSITIVE
2. NON-REDUCED SILVERSODIUMTHIOSULPHATE COMPLEXES IN POSITIVE
3. SOLUBLE SILVERSODIUMTHIOSULPHATE COMPLEXES + SILVER LOST IN THE PROCESSING SOLUTION
4. SILVERSODIUMTHIOSULPHATE COMPLEXES IN NEGATIVE
5. SILVER HALIDE
6. FOG

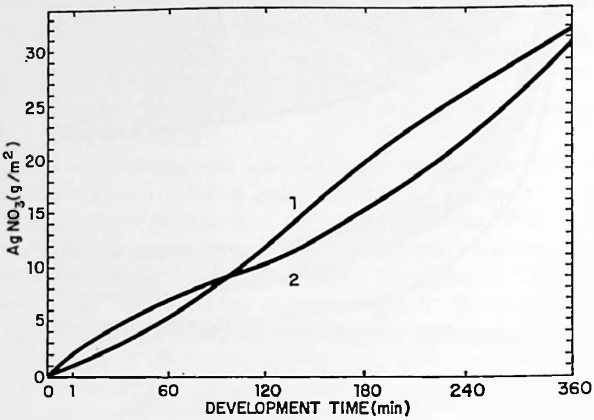
Fig. 4.16. Balance of silver distribution in material with nuclei on surface of layer.



SILVER DISTRIBUTION: NUCLEI IN THE LAYER

1. SILVER REDUCED IN POSITIVE
2. NON-REDUCED SILVERSODIUMTHIOSULPHATE COMPLEXES IN POSITIVE
3. SOLUBLE SILVERSODIUMTHIOSULPHATE COMPLEXES + SILVER LOST IN PROCESSING SOLUTION
4. SILVERSODIUMTHIOSULPHATE COMPLEXES IN NEGATIVE
5. SILVER HALIDE
6. FOG

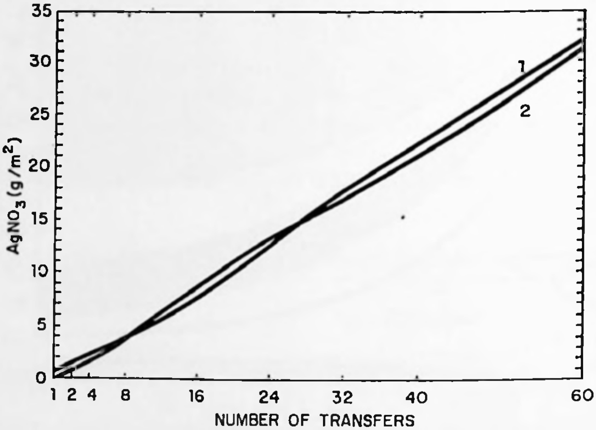
Fig. 4.17. Balance of silver distribution in material with nuclei within the layer.



PHYSICAL DEVELOPMENT

1.NUCLEI ON TOP OF THE LAYER
2.NUCLEI IN THE LAYER

Fig. 4.18. Effect of physical development on materials with different characteristics.



REPEATED TRANSFER

1.NUCLEI ON TOP OF THE LAYER
2.NUCLEI IN THE LAYER

Fig. 4.19. Effect of repeated transfer on materials with different characteristics.

The results given for the aluminium plate are not directly comparable with those given for the paper plate since the measurements were made under different conditions. In any case, the large differences between III and IV in the results given in columns B and C respectively show the lithographic effect clearly, as compared with the corresponding results in column A (nuclei in the layer) which do not differ from each other.

An examination was made in order to discover the reason for such a marked difference in the lithographic behaviour in the two cases.

The electromicrographs in Plate 4.3 show that the micro structures of the silver obtained in both the materials are almost the same. The physico-chemical behaviour of both the silver deposits was also investigated by studying the effect of physical development (see Figure 4.18) as well as by carrying out the DTR-process several times on the same surface (see Figure 4.19); but here again, no marked difference in physico-chemical behaviour could be found.

In Figures 4.16 and 4.17 a survey is given of the balance of silver in plates which were prepared by the DTR-process with the two types of positive material under investigation. It appears that with the plate with the nuclei on top, the negative retains a much larger amount of non-reduced silver hypo complexes and a much smaller amount of residual silver halide than the plates with the nuclei in the layer itself.

The presence of a positively charged silver complex positive appears to promote the oleophilic properties of the silver.

4.2.3 STRIPPING SYSTEMS. In these processes printing masters are prepared by the image-wise stripping out of the printing or non-printing areas in the receiving sheet.

Agfa AG[37] has patented the following process: a negative provided with a thin nuclei layer is pressed, after image-wise exposure, into contact with a hydrophilic colloid layer free from nuclei in the presence of a combined developer-fixer (Figure 4.20).

The DTR-process thus takes place in the negative material and changes the adherence of the image surface to the hydrophilic colloid layer in such a manner that the positive image areas, i.e. the nuclei enriched with silver, become strongly adherent whereas the negative image areas, in which the nuclei layer has remained unchanged, are still non-adherent as before.

When the negative is separated from the image-receiving material, the colloid in the "positive" material is stripped out and remains adhering to the negative in those areas which had been in contact with the non-exposed areas of the negative (Figure 4.21).

In this way, the positive material which was pressed against the negative is converted into a positively printing master in such a way that those image areas in the positive from which the hydrophilic colloid has been stripped out, are rendered oleophilic (the paper is more grease-receptive than the colloid)

whereas the remaining colloid areas are still hydrophilic (the printing master shows a certain resemblance to the graphic arts' offset deep printing plates in which the oleophilic printing elements are also situated in the lower layers.

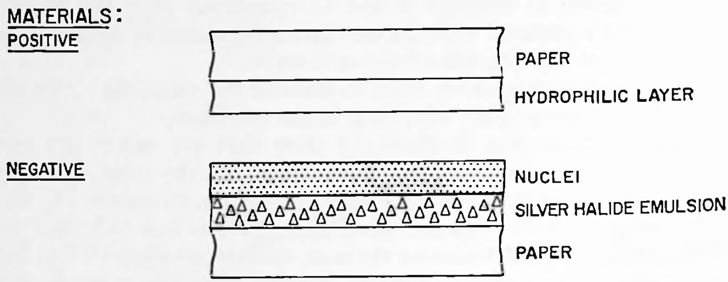


Fig. 4.20. Construction of material for Agfa stripping system.

Exposure: by the reflex or print-through contact method.
Processing: combined developer-fixer.

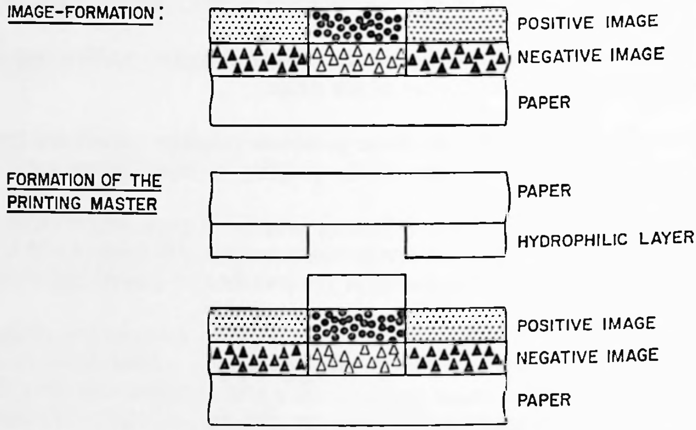


Fig. 4.21. Image formation and preparation of printing master by the Agfa system.

After-treatment: none.

A. B. Dick (U.S.A.)[38] proposes the following process: The image-receiving material consists of a hydrophobic support carrying a gelatin layer which contains an oxidizing agent in addition to nuclei. The silver image formed by DTR-processing now functions as a catalyst in the local disintegration of the gelatin by the oxidizing agent present, whereby the underlying oleophilic support is laid bare (Figures 4.22 and 4.23).

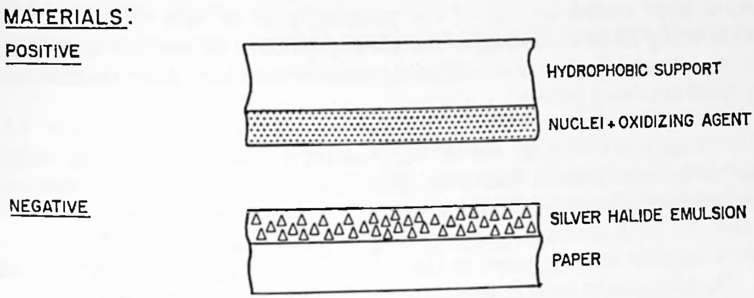


Fig. 4.22. Construction of material for A. B. Dick stripping system.

Exposure: by the reflex or print-through contact method.

Processing: (*a*) DTR-development; (*b*) washing off.

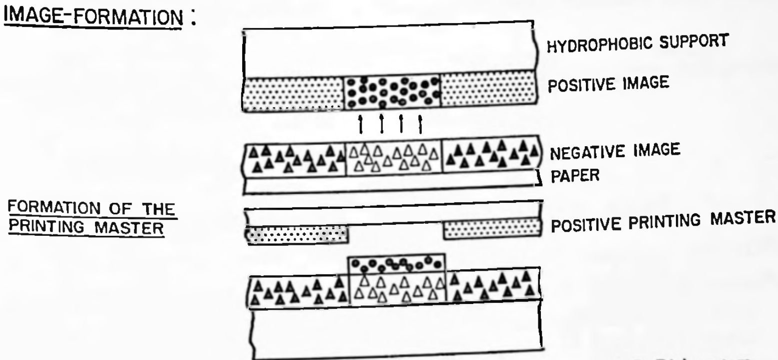


Fig. 4.23. Image formation and preparation of printing master by the A. B. Dick system.

After-treatment: none.

These materials will probably have little chance of being produced in practice since the oxidizing agents present cannot but strongly attack the nuclei. Moreover, no clear chemical explanation is forthcoming to account for the disappearance of the image elements in the printing areas (DTR-silver + binding agent).

4.3 *Monosheet systems for offset*

The DTR offset processes were so well received on the market as to lead to the development of offset materials in which the two DTR layers—i.e. the negative and positive layers—were united on one single support, with the

negative layer coated on top of the positive layer or vice versa, both these systems being known. Owing to the close proximity of the two active layers whereby lateral diffusion is considerably reduced the monosheet systems have a very good resolving power.

4.3.1 NEGATIVE LAYER ON TOP OF THE POSITIVE LAYER. A somewhat cumbersome monosheet process has been proposed by The Minnesota Mining & Manufacturing Company (U.S.A.).[39]

After the DTR-processing, the photographic emulsion is removed and the positive transfer image present in the underlying hydrophilic layer is bleached out. The hydrophilic layer in the image-areas is then removed so that the underlying hydrophobic layer is laid bare (Figures 4.24 and 4.25). In this way a positive printing plate is obtained since the bare hydrophobic support itself, owing to its highly oleophilic character, forms the printing areas whereas the neighbouring areas remain hydrophilic and therefore water-receptive. (These printing masters show a certain resemblance to offset deep printing plates.)

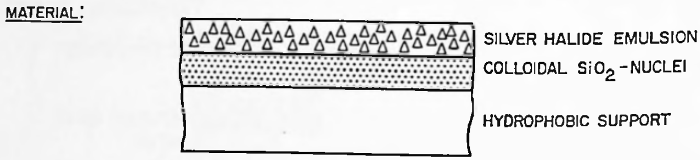


Fig. 4.24. Monosheet material for offset with negative layer on top.

Exposure: optically.

Processing: (*a*) DTR-development (30 sec); (*b*) washing off the negative layer by means of water (43°C — 20 sec); (*c*) bleaching out the positive image by means of potassium hexacyanoferrate(III) and potassium bromide; (*d*) rinsing and image-wise washing off the silicium oxide layer.

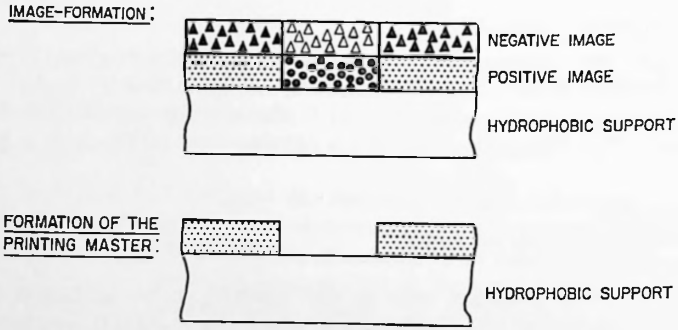


Fig. 4.25. Image formation and preparation of printing master on monosheet material with negative layer on top.

After-treatment: none.

It is not clear by what chemical mechanism the SiO_2 layer can be removed image-wise.

4.3.2 POSITIVE LAYER ON TOP OF THE NEGATIVE LAYER. The application of a very thin layer of nuclei on top of the hardened hydrophilic layer also has great advantages in the case of monosheet materials (Figures 4.26 and 4.27). Agfa-Gevaert have launched this technique under the trade name Rapilith.

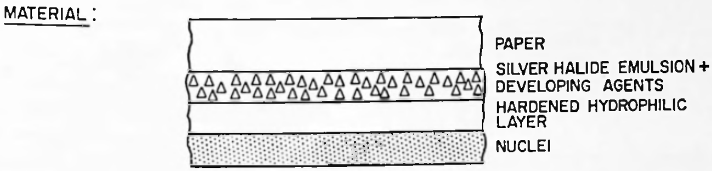


Fig. 4.26. Construction of Rapilith monosheet material with positive layer on top.

Exposure: optically.

Processing: DTR-development in an office duplicating machine with activator solution.

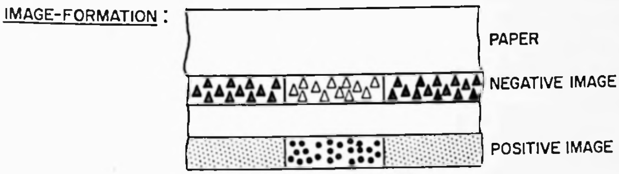


Fig. 4.27. Image formation on Rapilith material.

After-treatment: with a lithographic preparation.

In this case the emulsion layer can of course be of high sensitivity, enabling the exposure to the original to be made by means of a camera with mirror (see Figure 4.28).

This process can be made largely automatic which means that simply by pressing the button of the apparatus once, exposure and subsequent processing take place spontaneously and the process is rendered extremely suitable for continuous work.

The DTR-offset masters are intended for the reproduction of text and line images as well as of screen images. Plate 4.4 shows the reproduction of lines of 0·05 in. in width on an original, a printing plate and a print respectively as obtained with the process employing separate negative and positive materials (Copyrapid paper offset) and the monosheet process (Rapilith). From these figures it appears that in the last-mentioned process a resolving power of up

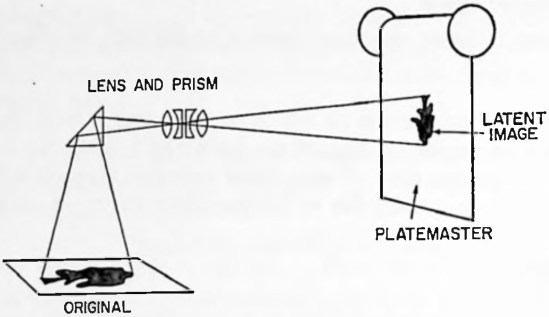


Fig. 4.28. With a highly sensitive emulsion, exposure to the original can be made by a camera with mirror.

to 120 lines per inch is possible whereas in the first mentioned process a resolving power of up to 165 lines per inch is obtained, these results are quite satisfactory.

4.4 *The economic aspects of diffusion transfer reversal offset printing*

Offset printing, which is a method derived from lithography, is based on the principle that water and fat repel each other. The uncovered non-printing parts of an offset printing plate accept water, whereas the image areas repel it. In a printing machine or duplicator the printing plate is first moistened with water by means of a roller and is then guided towards an inking roller. The moistened, uncovered parts of the printing plate repeal the greasy ink, whereas the unmoistened image areas accept the image. The ink image is transferred to the printing paper by means of a rubber roller.

A distinction should of course be drawn between the large offset machines used in the printing industry and small offset machines or offset-duplicators. The former are machines for producing runs of several hundred thousands and often millions of prints, and are capable of printing large formats as well as four-colour prints. As implied by their names, offset duplicators are intended for the duplication, i.e. the printing of relatively small quantities of documents of the formats which are commonly used in offices. Although, in principle, four-colour prints can be made by means of an offset duplicator, it is generally inadvisable to do this in practice.

DTR-offset printing forms part of the field of office duplicating, although the DTR-method can also be used for the production of printing plates of smaller formats in large-scale or industrial offset printing. As a matter of fact, in the United States local newspapers are printed from aluminium printing plates, the printing image of which has been formed by means of the DTR-method.

The office duplicating market is older and larger than the office copying market and moreover it is still growing considerably. At present in office duplicating, mainly four duplicating techniques are employed in addition to a few less important processes.

These four duplication techniques consist in the use of (*a*) spirit-duplicators, (*b*) stencil-machines, (*c*) offset-machines, and (*d*) xerographic machines respectively.

Duplication by means of spirit-duplicators on the one hand and by means of stencil-machines on the other hand are both long-established methods, by means of which rather limited quantities of duplicates can be made comparatively cheaply.

The production of copies by means of alcohol duplicators, is the cheapest method but the image quality is not particularly good and the runs are limited to a few hundred copies.

With stencil machines several thousands of copies can be produced at a low price, although this is somewhat higher than that of spirit-duplicators. Nevertheless, the image quality of these copies is definitely inferior to that of the offset copies.

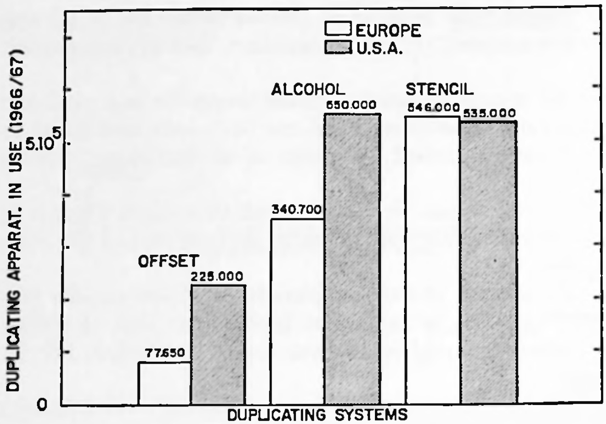
Xerographic duplicating machines are the only ones which function without a master copy. In fact they are copying machines which deliver copies continuously at a high rate (60 copies per minute) as compared with most copying machines, but at a relatively low rate as compared with offset duplicators. The quality of a xerographic duplicate is better than that of a stencil copy, but is inferior to that of the average offset duplicate. A xerographic duplicate can be made easily and the process itself does not suffer from contaminating influences, but the price of a copy is very high.

The offset method is considered to be the most flexible duplicating method; at the same time it yields the best results and the longest runs. Moreover, offset duplicators operate at relatively high rates (up to 10,000 duplicates per hour).

At present there are approximatively a dozen different processes for the production of masters for offset duplicators. Some masters are so cheap, that they can be used economically for runs of only a few dozen prints. The quality of other masters is so good, that they are capable of reproducing screen images very well, and thus can be employed with optimum results in four colour-printing. They can also be relied on to give long runs of at least 100,000 prints.

Before considering more fully the part played by the DTR-method in the offset duplicating field, we shall first give some figures which underline the economic importance of the most important duplicating methods. Since xerographic duplicating machines were not yet available in Europe when the information given in the Figure 4.29 was compiled, they are not included in the charts showing apparatus in use and copies produced. The charts comprise

data obtained from the results of market research carried out during the period 1966–67 in the United States and in 10 European Countries (Germany, the



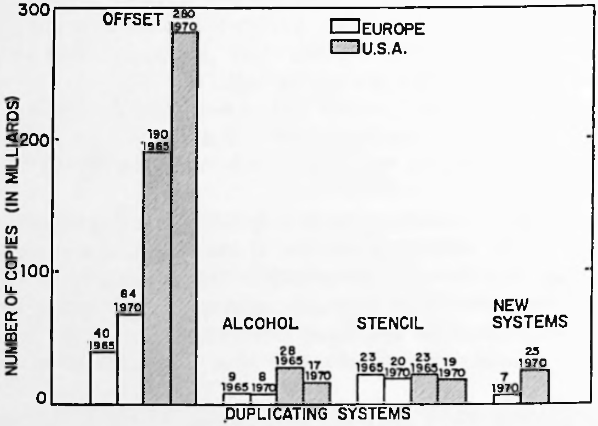
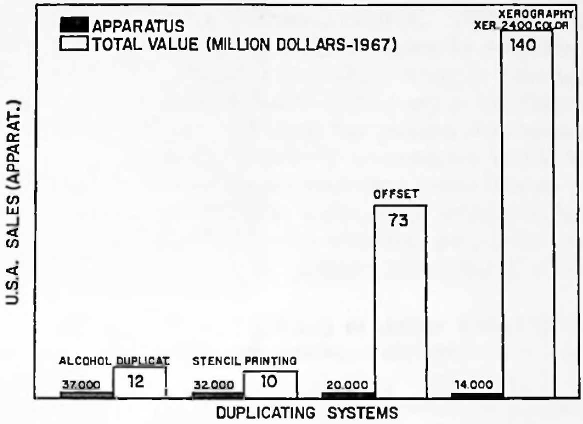


Fig. 4.29. Relative economic significance of the most important duplicating methods in 1966/7.

United Kingdom, France, Italy, Switzerland, Sweden, Belgium, the Netherlands, Denmark, and Norway).



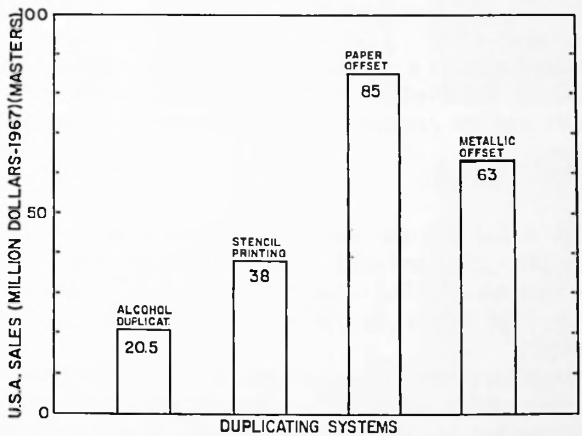


Fig. 4.29 (*contd.*).

The importance of the office duplicating market is seen very clearly from these tables. In 1967 the total sales in the United States reached $1,510,000,000.

Experts estimate that the sales will have doubled by 1972. No exact data of world sales are available. However, it is estimated that they will reach 5 billion dollars by 1972. In this connection it may be added that the ever-growing distribution of table-top offset duplicators will very probably put a brake on the sales of spirit duplicators and stencil machines. On the other hand, the conditions in the United States seem to indicate that the growing success of xerographic copying and duplicating machines will have no adverse effect on the further development of offset duplicating.

The question now arises as to how the DTR-methods for the production of masters stand in relation to the whole of offset duplicating. Without entering into technical details, we shall now state the different methods of making an offset master for a duplicating machine:

1. By directly typing, writing or drafting on a paper printing plate;
2. By means of a xerographic machine, the xerographic copy being used as a master;
3. By means of an Electrofax-machine, the electrocopy being used as a master;
4. By exposure and "activation" of a twin-layer silver salt emulsion on a waterproof paper support (Verilith process);
5. By exposure and "development" of a silver salt layer on a plastic support (3M-process);
6. By a contact print of a negative or a positive on a pre-sensitized plate;
7. By a master sheet, which together with a sheet of paper carrying a wax layer, and the original, is passed through a thermographic copying apparatus;
8. By the DTR-method.

There is no doubt that the method using pre-sensitized plates produces masters of the best quality and the longest runs. On the other hand these plates are very expensive, an extra film is needed for the production of an intermediate negative or an intermediate positive, and the production of a master takes quite a long time.

The xerographic and electrophotographic methods yield masters which are medium or lower quality, but which can be made ready very rapidly.

The Verilith-method has the advantage of being simple and convenient and moreover of yielding good quality masters. The requisite special apparatus is however rather expensive.

The thermographic method is fairly cheap, but the quality of the masters is somewhat inferior. Moreover, only originals which absorb infra-red light can be reproduced.

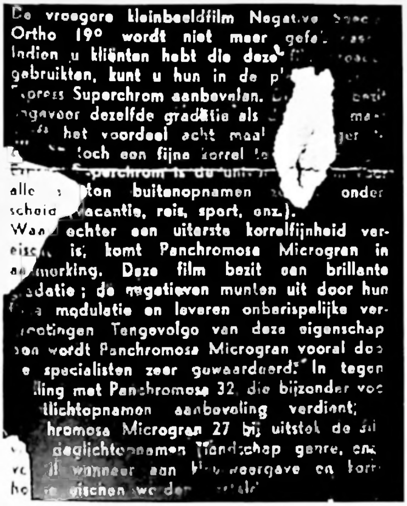
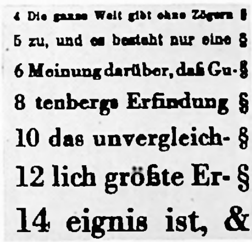

De vroegere kleinbeeldfilm Negative ...
Ortho 19° wordt niet meer gefa...
Indien u kliënten hebt die deze f...
gebruikten, kunt u hun in de p...
...press Superchrom aanbevelen. ...
...gevoer dezelfde gradatie als ...
... het voordeel acht maal ...
... toch een fijne korrel ...
... Superchrom is de uni...
alle ... ten buitenopnamen ... onder
scheid ... vacantie, reis, sport, enz.).
Waar echter een uiterste korrelfijnheid ver-
eist is, komt Panchromosa Microgran in
aanmerking. Deze film bezit een brillante
gradatie; de negatieven munten uit door hun
... modulatie en leveren onberispelijke ver-
grotingen. Tengevolge van deze eigenschap
... wordt Panchromosa Microgran vooral do...
... specialisten zeer gewaardeerd. In tegen...
...ling met Panchromosa 32 die bijzonder vo...
... lichtopnamen aanbeveling verdient;
...hromosa Microgran 27 bij uitstek de ...
daglichtopnamen (landschap genre, enz.
... wanneer een ... weergave en korr...
... eischen worden ...

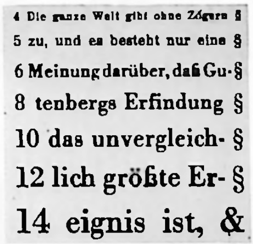
Plate 1.1 Birth of the DTR process. The attempt to produce a right-reading negative by a stripping process was frustrated by the emulsion layer coming away from the paper during the fixing process. The clear positive image that appeared under the negative layer, however, led to the discovery of a new process.


4 Die ganze Welt gibt ohne Zögern §
5 ... es besteht nur eine §
6 ... darüber, daß Gu- §
... Erfindung §
... unvergleich- §
... größte Er- §
... ist, &

25%

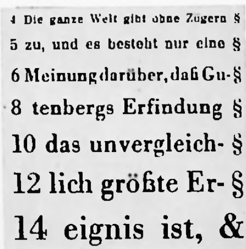

4 Die ganze Welt gibt ohne Zögern §
5 zu, und es besteht nur eine §
6 Meinung darüber, daß Gu- §
8 tenbergs Erfindung §
10 das unvergleich- §
12 lich größte Er- §
14 eignis ist, &

20%


4 Die ganze Welt gibt ohne Zögern §
5 zu, und es besteht nur eine §
6 Meinung darüber, daß Gu- §
8 tenbergs Erfindung §
10 das unvergleich- §
12 lich größte Er- §
14 eignis ist, &

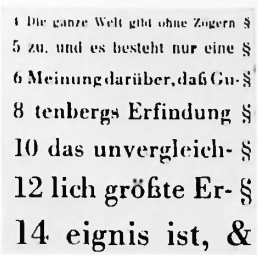
12%

Under-exposure

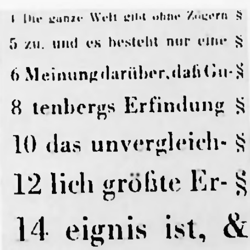

4 Die ganze Welt gibt ohne Zögern §
5 zu, und es besteht nur eine §
6 Meinung darüber, daß Gu- §
8 tenbergs Erfindung §
10 das unvergleich- §
12 lich größte Er- §
14 eignis ist, &

Correct exposure

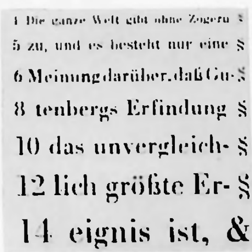
Plate 3.1 Exposure latitude in the case of Copyrapid material.


4 Die ganze Welt gibt ohne Zögern §
5 zu, und es besteht nur eine §
6 Meinung darüber, daß Gu- §
8 tenbergs Erfindung §
10 das unvergleich- §
12 lich größte Er- §
14 eignis ist, &

15%


4 Die ganze Welt gibt ohne Zögern §
5 zu, und es besteht nur eine §
6 Meinung darüber, daß Gu- §
8 tenbergs Erfindung §
10 das unvergleich- §
12 lich größte Er- §
14 eignis ist, &

25%


4 Die ganze Welt gibt ohne Zögern §
5 zu, und es besteht nur eine §
6 Meinung darüber, daß Gu- §
8 tenbergs Erfindung §
10 das unvergleich- §
12 lich größte Er- §
14 eignis ist, &

35%

Over-exposure

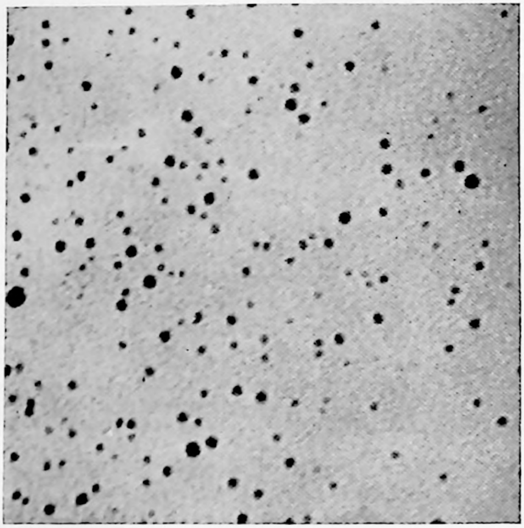


Plate 3.2 Electronmicrograph (300,000 ×) from which it was possible to derive a mean diame[illegible] about 45 Å for silver sulphide and nickel sulphide nuclei.

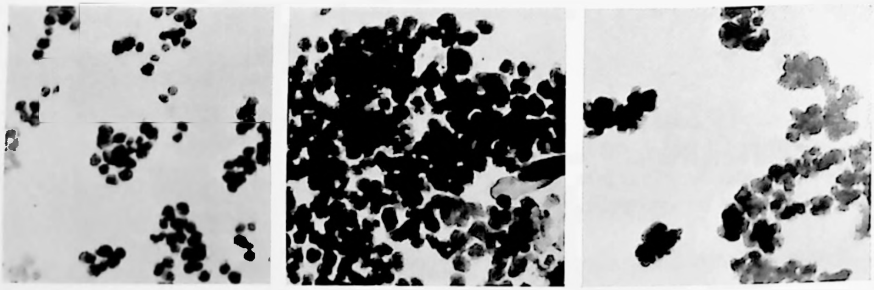


Plate 3.3 (*left*) Image silver without additives. Electron microscope (80,000 ×).
Centre Image silver after addition of 137·5 × 10^{-3} mmol of 1-phenyl-2-imidazolidine-thione. Electron microscope (80,000 ×).
Right Image silver after addition of 330 × 10^{-3} mmol of 6-methyl-perhydro-1,3-thiazine-2-thione. Electron microscope (80,000 ×).

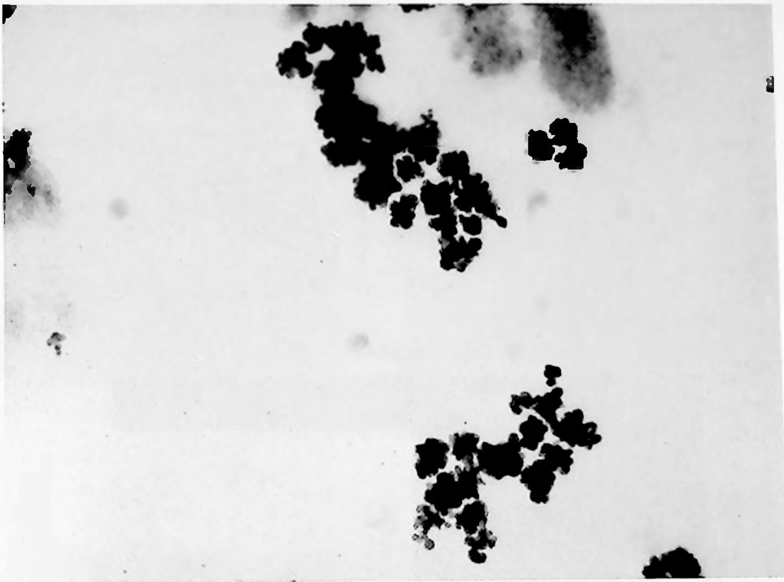


Plate 3.4 Electronmicrograph of grain structure of Copyrapid conventional material.

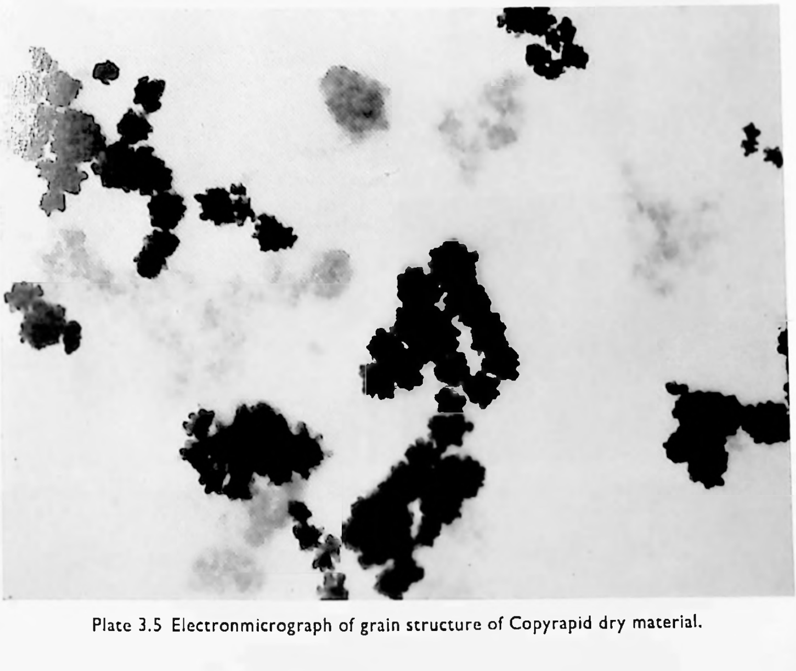


Plate 3.5 Electronmicrograph of grain structure of Copyrapid dry material.

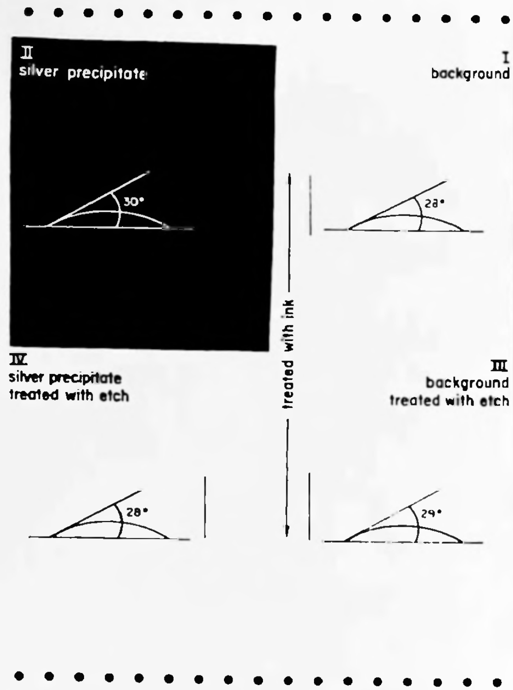


Plate 4.1 Ink receptivity of positive material with nuclei in a hydrophilic layer.

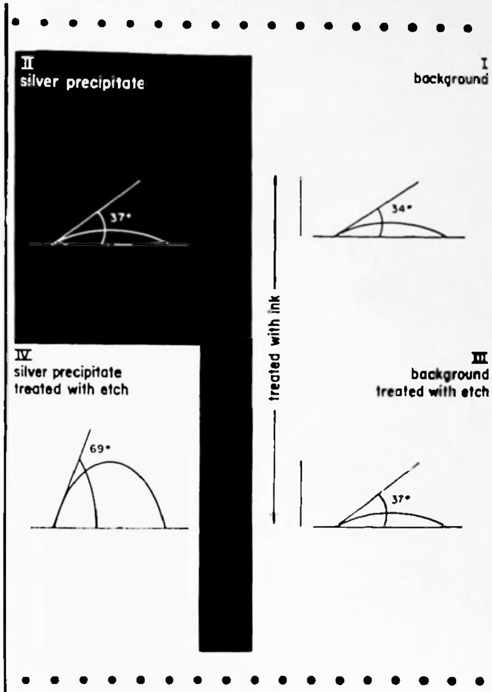


Plate 4.2 Ink receptivity of positive material with nuclei in a very thin top layer.

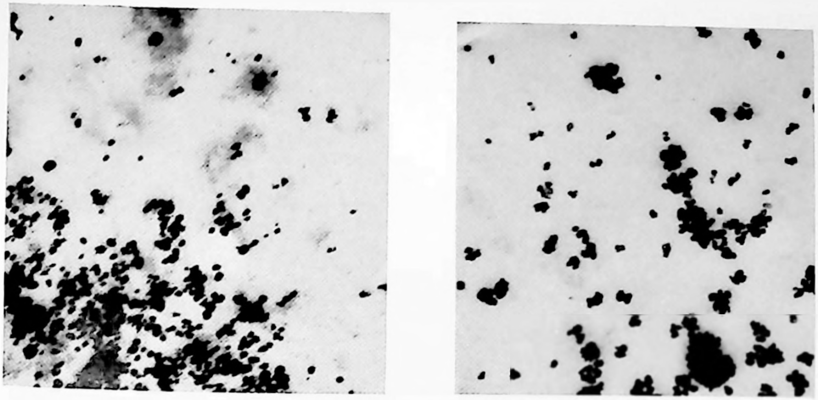


Plate 4.3 *Left* Paper offset nuclei in the layer. *Right* Paper offset nuclei on top.

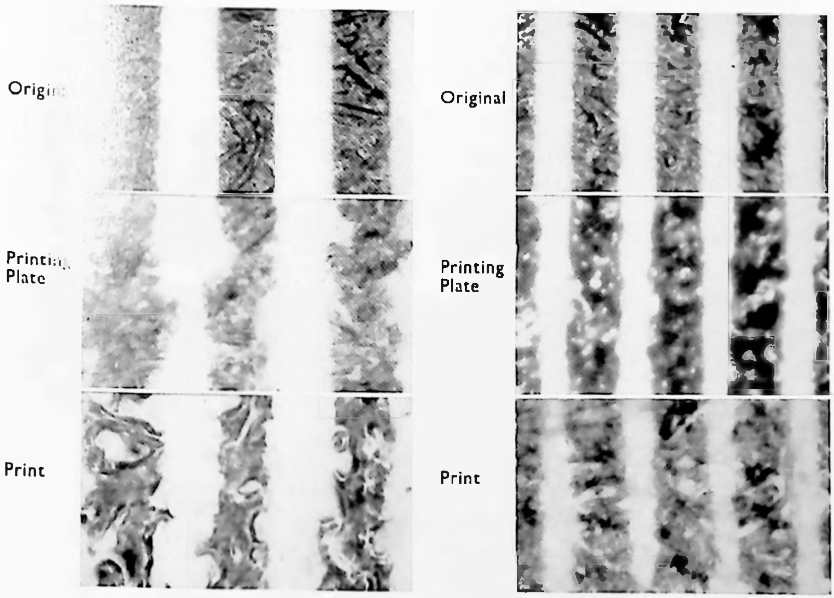
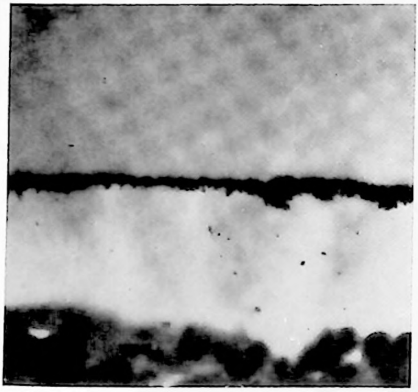


Plate 4.4 *Left* Copyrapid paper offset 120 L/in. screen (enlarged 80 ×). *Right* Rapilith 165 L/in. screen (enlarged 80 ×).



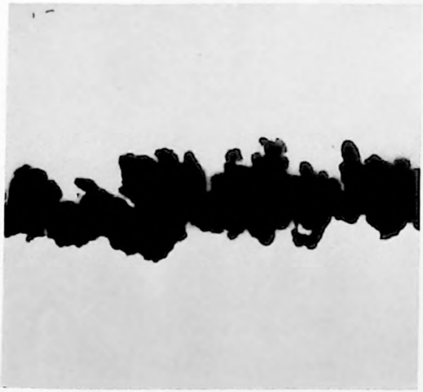


Plate 5.1 Electron microscope reproductions of sections obtained in a Carborapid model experiment. *Top left* Silver produced by reduction in unexposed areas and deposited in nuclei layer. *Bottom* Partial enlargement of previous image. *Top right* No silver is deposited in the nuclei layer in the exposed areas of the negative.

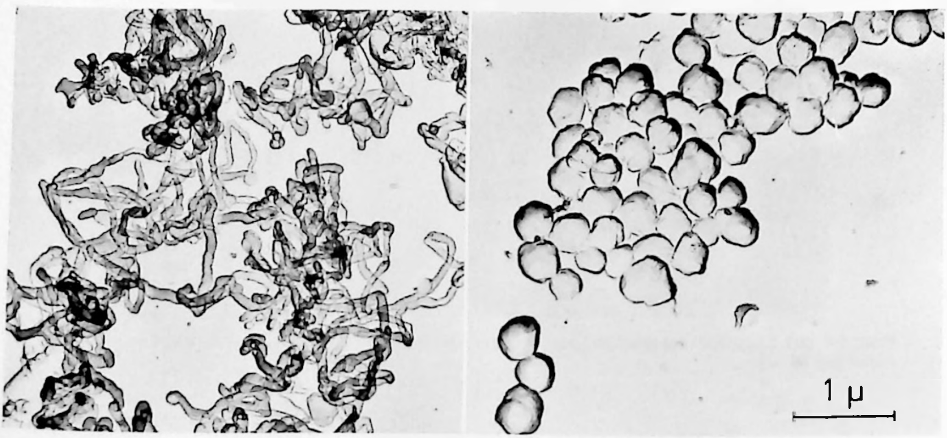


Plate 6.1 Shape of silver particles developed by chemical development (left-hand side—filamentary) and by physical development (right-hand side—spherical). Taken from E. Klein and R. Matejec, 100 *Jahre Photogr. Ges. in Wien* (Centenary of the Vienna Photographic Society), Pub: O. Helwich, Darmstadt and Vienna, 1961.

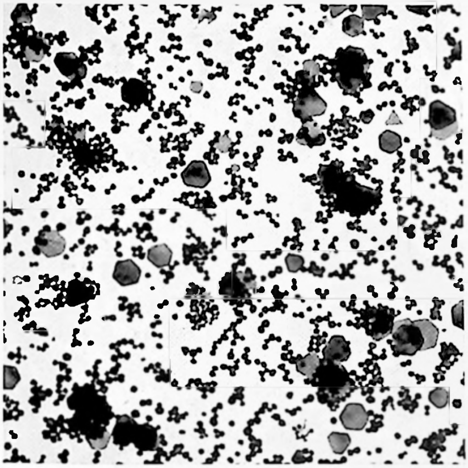


Plate 6.2 Growth of silver on silver sulphide nuclei, shadowed with gold ($\alpha = 15°$), enlarged 10,000 ×.

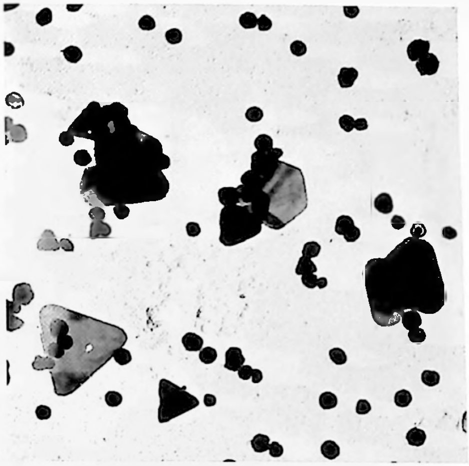


Plate 6.3 Yellow silver sol after reduction of the silver thiosulphate (conc. of nuclei $2{\cdot}8 \times 10^{-5}$ mole/l) $tg\alpha = 1/4$, enlarged 30,000 ×.

Plate 6.4 Blue silver sol after reduction of the silver thiosulphate (conc. of nuclei $2{\cdot}8 \times 10^{-5}$ mole/l) $tg\alpha = 1/4$, enlarged 10,000 ×.

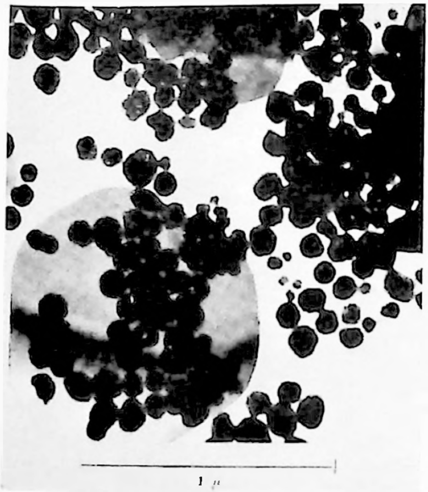


Plate 6.5 Electron micrograph of silver developed without a toner

Plate 6.6 Electron micrograph of silver developed in the presence of III, 2 mg/l

Plate 6.7 Electron micrograph of silver developed in the presence of II, 3 mg/l

Plate 6.8 Electron micrograph of silver developed in the presence of II, 10 mg/l

The 3M-method mentioned under (5) gives good results, but the cost of the materials is rather high and the runs are somewhat limited. The method described under (1) (direct typing or writing on a paper master) is, of course, the simplest and cheapest one, but it has obvious limitations.

Finally, there is the DTR-method with its many variants. In general the DTR-method has not earned the popularity which it actually deserves.

As a matter of fact, every owner of a DTR-copying apparatus can use this same apparatus for the production of paper offset masters. Consequently, the cost of the apparatus is naturally very low. Besides, the print quality is very good, and screen images can be reproduced fairly well. The DTR aluminium printing plate gives quite long runs (of at least 10,000) and the plates can be prepared rapidly (30 sec to 1 min).

The more widespread use of the DTR process for copying in offices may possibly have drawn the attention of manufacturers to the use of DTR materials in this field since from the commercial point of view the DTR offset printing sheet had formerly been regarded as having been somewhat superseded by other materials. The present developments taking place on the office copying and office duplicating markets enable it to be said that these manufacturers will pay increasing attention to perfecting and promoting the sales of DTR systems for the production of offset masters.

Thus it can be foreseen, that in the future these methods will occupy a more important place on the office duplicating market than that which they occupied hitherto.

In this connection we would refer to the end of the chapter headed "The commercial aspects of the DTR-process" in which the new DTR-offset masters have been discussed. From what has been said there, it can be concluded that the aims of the manufacturers of DTR-material for offset duplicating are two-fold. In the first place attempts are being made to enable an offset master to be produced as simply and cheaply as possible (see the DTR-monosheet offset system and the DTR-paper offset master). Used in combination with table-top office printing machines, these simple and cheap masters may contribute to the foreseen and fast expansion of the office duplicating market. In the second place efforts are being made to enlarge the potentialities of offset printing with DTR aluminium plates by the wider distribution of development-transfer apparatus equipped with a register unit. As mentioned before small local newspapers in the United States print by means of DTR-aluminium plates. This foreshadows a larger application of these plates (in addition to their use in office duplicating) for small-scale operations in ordinary commercial printing offices.

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V. OTHER SYSTEMS

5.1 *Monosheet systems for reprography*

It may be said that the inventors of the DTR system have from the very beginning thought of two active layers, a light-sensitive layer and an image-receiving one, both coated on the same support (cf A. Rott: "Un nouveau principe de l'inversion", *Sci et Ind. Phot.* (1942, p. 151).

The easiest way to work this idea out was to coat successively an image-receiving layer, insoluble in warm water and containing developing nuclei, and a non-hardened silver halide emulsion.

After exposure and development, a negative image is obtained in the light-sensitive emulsion layer while the corresponding positive image is diffused into the image-receiving layer. After removal of the upper layer, e.g. by means of warm water, the positive image appears.

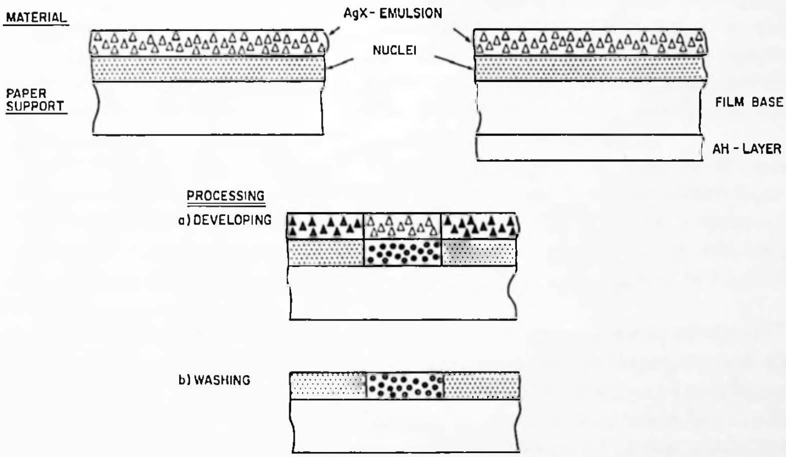

Fig. 5.1. Construction and processing system of materials based on removal of negative layer.

The remarkable commercial success of the DTR-system brought numerous requests for simplified materials, from which the negative layer need not be removed.

These materials can be broadly classified as follows: the first group includes materials which require separation of the negative from the positive layer after

processing; the second group comprises materials which have been simplified to such an extent that the light-sensitive layer need no longer be removed.

5.1.1 SYSTEMS BASED ON THE REMOVAL OF THE NEGATIVE LAYER. An early example in this field was the "Diaversal"-paper of Gevaert Photo-Producten N.V., Belgium (Figure 5.2). This material was used for making enlargements directly from (colour) transparencies (A. Rott, "Een nieuw fotografisch omkeer-procédé, Diaversal" (A new photographic reversal process, Diaversal), *Nederlands Jaarboek voor Fotokunst*, 1948–49, p. 32).

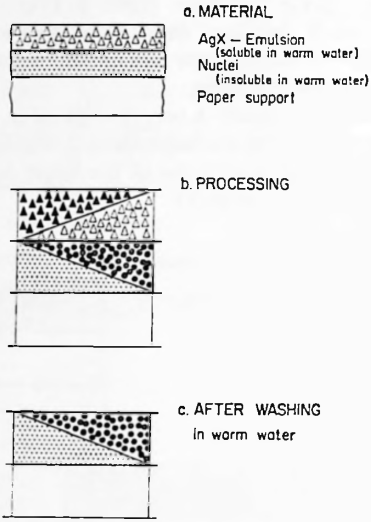

Fig. 5.2. Treatment of the "Diaversal" enlarging paper.

Though the processing was rather complicated, because a transfer and a toning bath were required as well as a developer, this enlarging paper proved fairly successful in the period 1946–49.

Black-and-white enlargements of transparencies were, in contrast with the latter, characterized by fairly good keeping qualities and consequently perfectly suited for archives and filing purposes.

As to the reproduction system, there are now the following DTR-materials on the market:

Eastman Kodak Company: Autopositive Projection Paper
Agfa-Gevaert AG: Autoreversal Rapid AR90-paper

Direct positive film for document copying cameras:

Kodak: Autopositive Projection Film
Agfa-Gevaert AG: Autoreversal Rapid AR1pm Film.

5.1.1.1 *Material composition.*

Exposure: optically, by means of a prism or reversing mirror in order to produce non-laterally reversed images.
Processing: (*a*) development in a high-contrast developer containing hypo; (*b*) rinsing with water, to remove the silver halide emulsion.

5.1.1.2 *Resulting Image.* The positive image formed is rich in contrast and possesses a resolving power, which is equivalent to that of photographic emulsions of the same speed.

Although the positive image is formed by the same chemical mechanism as that which governs other DTR-processes, washing after processing, not only fulfils its actual purpose, i.e. the removal of the light-sensitive layer, but it also increases the stability of the image considerably.

5.1.1.3 *Image-receiving layer.* The image-receiving layer of these materials is composed of a hydrophilic binder, which allows the ions to diffuse in an aqueous medium, and of substances, which are either development nuclei for the physical development of the positive image or are capable of forming a dark-coloured silver deposit with the diffusing silver complex ions. Development nuclei which are commonly used are colloidal silver, silver sulphide,[1] nickel sulphide, cobalt sulphide, manganese sulphide, zinc sulphide, zinc selenide, or zinc telluride.[2] These nuclei are capable of being adsorbed to inert solid particles,[3] which themselves are dispersed in the binder.

Since from the very moment of the manufacture of the material the silver halide emulsion is in contact with the image-receiving layer, the nuclei have to be photographically inert and consequently practically insoluble in water.

Moreover, measures should be taken to render the binder of the image-receiving layer insoluble in the processing solutions by giving it a suitable hardening treatment.

5.1.1.4 *Development.* After image-wise exposure of the silver halide emulsion, the material is developed in a developer which is comprised substantially of developing agents, alkaline components, and a silver halide solvent, which is usually sodium thiosulphate. The developer is protected from oxidation by the addition of reducing agents such as sodium sulphide. Retarding agents such as potassium bromide prevent the silver halide emulsion from excessive fogging.

During development, the same partial processes take place in monosheet materials as in two-sheet DTR materials. In the unexposed areas, the dissolved silver complexes diffuse into the developer as well as into the image-receiving layer, so that only a part of the silver in the negative emulsion is available for the formation of the positive image. This lower yield of silver should be taken into account when planning a monosheet material.

5.1.1.5 *The removal of the silver halide emulsion layer.* As soon as the positive image is formed, the light-sensitive layer must be removed. According to the earliest patents,[1,4] this can be accomplished by washing with warm water, dissolving, stripping off, or by the use of a chemical process. The most obvious medium in which this can be performed, is water, which moreover also frees the image-receiving layer and occasionally also the support from residual developer.

In the simpler embodiments, gelatin is used as the binder for the image-receiving layer as well as for the silver halide emulsion layer. Effective removal of the emulsion is only possible if a specific hardening agent is used to render the image-receiving layer, but not the emulsion layer, insoluble. As it is very difficult, however, to harden a gelatin layer without also to some extent hardening the adjacent gelatin layer, various means have been devised for enabling the emulsion layer to be removed without any difficulty.

In order to make this step in the process proceed more easily, a thin layer of a hydrophilic colloid can be provided between the image-receiving layer and the emulsion layer. This colloid, e.g. starch[1] or methylcellulose[5] is usually incompatible with gelatin and does not react with the hardening agent added to the image-receiving layer. There is a danger however, that the emulsion may lose contact during the development and before the positive image has formed completely. This loss of close contact between the two layers concerned is obviously irreparable and gives rise to very disturbing image effects.

This aspect of the matter becomes still more pressing in the mechanical treatment in which, after exposure, the paper is conducted automatically through the developer in which the emulsion, in its wet condition, must be capable of resisting any friction between it and the guide elements, as is the case for instance in certain document copying cameras.

It was found that the intermediate layer could be composed of special hydrophilic colloids, the swelling capacity of which in developing baths is restricted considerably by the addition of mineral salts.[6] When a considerable quantity of an alkaline substance, e.g. sodium phosphate is added to the developer, an intermediate layer consisting of polysaccharide hydroxyalkyl ethers will remain in a very compact condition. However, as soon as the material is brought into the rinsing water and the concentration of sodium phosphate decreases, the intermediate layer begins to swell and repels the emulsion spontaneously.

After development, the emulsion can be treated with solutions of substances, which lower the melting point of the gelatin,[7] e.g. potassium thiocyanate and aryl sulphonates, and this enables the emulsion to be removed afterwards at room temperature. Similar substances, e.g. urea, can also be added previously to the emulsion. Moreover these substances neutralize the hardener which diffuses from the image-receiving layer.[8]

An alternative solution to this problem of removing the negative layer is to use different binders for the image-receiving and the silver halide emulsion

layers respectively, choosing binders which are immiscible. The first layer may, e.g. be composed of gelatin whereas the second may consist substantially of polyvinylalcohol or its acetal. Another embodiment in accordance with which the respective binders are permuted is equally possible.[9] It may be observed in passing that, in many cases, polyvinyl alcohol may restrain the formation of a DTR image.

In this connection other photographic emulsions have been worked out; the binder in these emulsions consists mainly of polymers which are soluble in alkali, e.g. polyvinyl alcohol, cellulose methyl ether,[10] the polyvinyl esters of dicarboxylic acids such as polyvinyl maleate and polyvinyl phthalate, polystyrene sulphonic acid,[11] the dicarboxylic acid esters of cellulose derivatives such as, e.g. ethylcellulose phthalate,[12,13,14] and the cellulose esters of sulphoarylcarboxylic acids such as ethylcellulose sulphobenzoate.[15]

Photographic emulsions containing such synthetic substances as binding agent differ from the usual gelatine emulsions in that they do not gel on cooling. During the coating of these emulsions it is therefore necessary to bring about gelation by other, mainly chemical means. For instance polyvinylalcohol emulsions are made to gel by the addition of, e.g. borax to the subjacent layer. Acid cellulose ethers are made to gel by bringing them into contact with layers which contain acids, e.g. citric acid or salts of polyvalent metals such as calcium actinate, aluminium nitrate, cadmium actinate, magnesium chloride, etc. Some cellulose ether derivatives can be made to gel by merely heating them.

In the case of emulsions, the binder in which dissolves in the rinsing water, there is a risk of the developed silver grains in the negative image being set free and setting down in the white areas in the final positive. These grains can be removed by rubbing the positive while it is still wet although this procedure is rather inconvenient in automatic processing systems. The formation of such undesired deposits can be counteracted by providing a special intermediate layer between the image-receiving layer and the emulsion layer, which intermediate layer is also soluble in water after development.[5,13]

On the other hand part of the water-soluble binder can be replaced by a colloid, e.g. gelatin, which is insoluble at room temperature. The proportion can be adjusted in such a way, that the emulsion does not dissolve, but is set free in the form of very small flakes in which the negative silver is taken away integrally.[11,15]

It is also possible to remove the negative emulsion mechanically. In one of the basic patents covering the DTR process[1] a description is given of a method of pressing the negative emulsion into contact with an inert auxiliary support after development and of stripping off the negative emulsion by means of this support. Thus it is possible to produce simultaneously in one recording a positive as well as a negative image.

Later it was realized that the auxiliary support could also be provided with the requisite reagents for development, e.g. alkali, a silver halide solvent, and

water-retaining substances, whereas the developing agents could be incorporated in the negative emulsion.[16] According to another variant, the auxiliary support was soaked previously with a developer or activator solution, thus creating a semi-dry process.[17]

The aim of most practical copying processes is the immediate production of

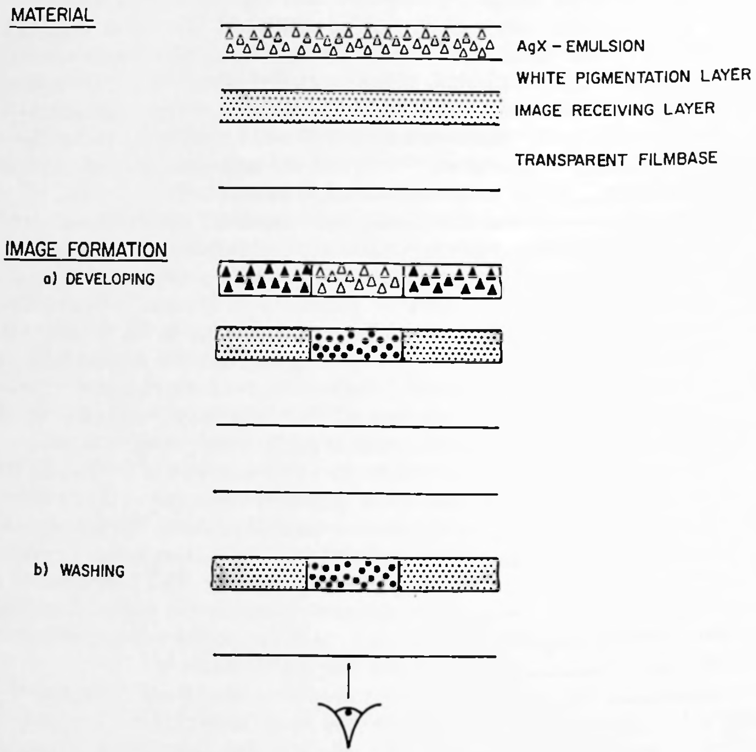

Fig. 5.3. Special material for reflex exposure with separate layer containing a white pigment.

a neutral black image or even a blue-black image. Thus it is obvious that all the means employed for producing a neutral or blue-black image tone in two-sheet DTR processes are equally applicable to the monosheet systems provided however, that they do not adversely affect the photographic emulsion during storage.

Certain ingredients have therefore been described for specific applications solely in monosheet systems. For instance 1,2,3-oxadiazolethiols, 1,3,4-thiadiazolethiols, 2-benzothiazolinethione and xylenesulfonic acid, these products

being used alone or together or in combination with 1-phenyl-1H-tetrazole-5-thiol which is often used[13] are incorporated in the negative layer of a monosheet material.

Another patent describes a monosheet material, the image-receiving layer of which contains an unusually high concentration of blue-toning agents containing mercapto, e.g. 5 to 25 g of mercapto compound per g of available silver.[18] In

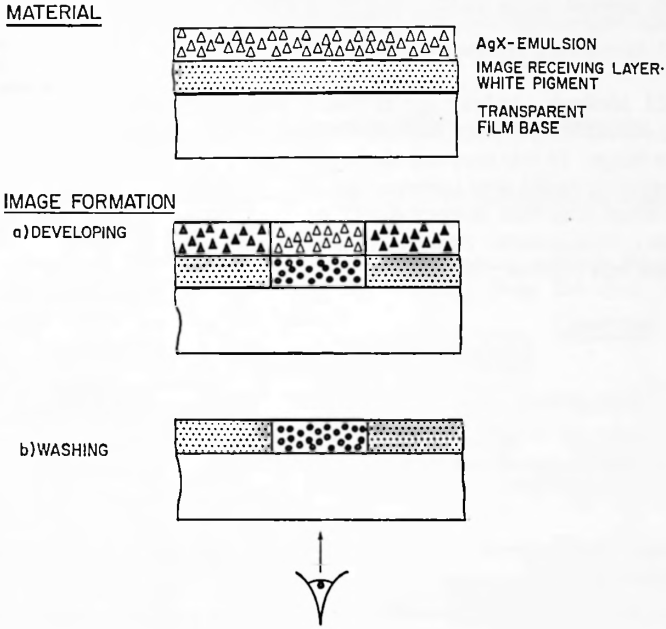

Fig. 5.4. Simplified reflex material with white pigment included in the image-receiving layer.

this way, not only is a black image tone obtained, but the material also acquires an excellent steep positive gradation, which is admirably suited to line and screen recording.

When the negative emulsion of a monosheet material is given a reflex exposure as described above, a laterally reversed mirror image is obtained in the negative layer as well as in the image-receiving layer. In practice therefore the document copying camera must be equipped with a reversing prism or a reversing mirror. A reflex exposure of the negative emulsion with the latter in contact with the original naturally yields a laterally reversed image.

A material of the following special composition enables a reflex exposure to be made. A transparent support is coated consecutively with an image-receiving

layer, a layer containing a white pigment, and a detachable silver halide emulsion layer. The emulsion layer is exposed in contact with the original. After-development and removal of the emulsion layer, the positive image is visible through the transparent support (Figure 5.3).[8]

In a simplified embodiment the image-receiving layer already contains the white pigment, thus eliminating one layer (Figure 5.4).[19]

5.1.2 MONOSHEET SYSTEMS IN WHICH THE NEGATIVE IS NOT REMOVED

5.1.2.1 *Methods.* As long ago as 1942 a description was given of material[20] with an emulsion layer which contained the requisite ingredients for build-up of a positive image. In this material, the ingredients necessary for development and the developing nuclei were incorporated in one single layer. During processing, all the silver salts were converted into silver either during the primary or the secondary development. Apart from a short rinse in water no supplementary treatment was necessary (Figures 5.5, 5.6).

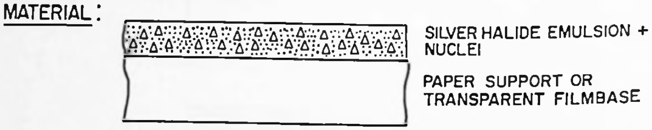

Fig. 5.5. Material with ingredients for development and developing nuclei in one layer.

Exposure: Optically by means of a mirror or by print-through contact with an original printed on one side.

Processing: Developing and transfer in a developer solution containing sodium thiosulphate.

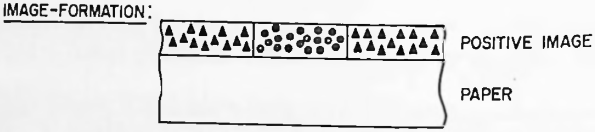

Fig. 5.6. Image formation in single-layer material.

The image formation is based on the difference in the covering power of the primarily and the secondarily developed silver. If the light-sensitive layer contains only a small amount of silver halide the silver formed during the primary development has only a reduced covering power whereas that formed by

the DTR-development reveals a large covering power. The image contrast which is obtained greatly surpasses in quality that which is required in practice.

In 1949 a process was described for making line images by the diffusion of non-complexed ions (Figure 5.7, 5.8).[21,22]

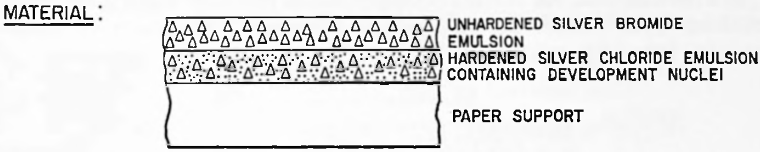

Fig. 5.7. Material for making line images by diffusion of non-complexed ions.

Exposure: Optically by means of a mirror or by print-through contact with an original printed on one side.

Processing: Development in a developer containing soldium thiosulphate but no potassium bromide; fixing; washing away the silver bromide emulsion by means of hot water.

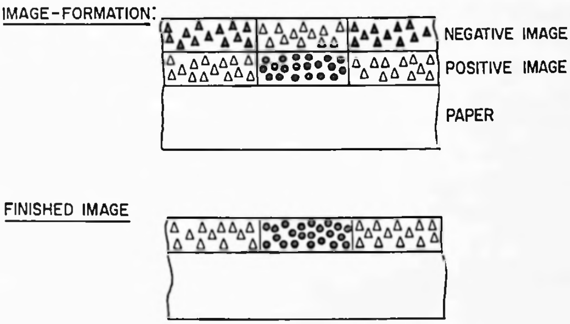

Fig. 5.8. Image formation by diffusion of non-complexed ions.

Finished image: During development, the silver bromide is reduced to silver in the exposed areas. The bromine ions thus liberated inhibit the local development of the subjacent silver chloride emulsion. In the unexposed areas the silver bromide is not reduced, whereas the subjacent silver chloride is reduced. For the development of the image, an incomplete DTR process is used here, because there is practically no transfer of silver salts from one layer to the other. The development of the negative image inhibits the spontaneous DTR development of the subjacent silver chloride

layer in the exposed areas, but not in those areas which still contain unexposed silver. The advantage of this material is its high sensitivity. A disadvantage, however, is that the material has to be fixed prior to or subsequent to the removal of the uppermost emulsion layer.

In a third method, one side of the support can be provided with a silver halide emulsion layer, whereas the other side of the support may carry an image-receiving layer (Figure 5.9).[23,24,25]

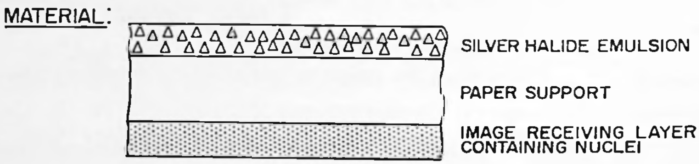

Fig. 5.9. Material with layers on both sides of support.

Exposure: Reflex or by print-through contact.

Processing: Development in a developer containing sodium thiosulphate and transfer after winding the material on to a spool. During the winding operation the front-surface comes into contact with the back surface which carries the image-receiving layer, thus enabling image formation by diffusion to take place. The resulting positive image made its appearance during the winding operation. This special embodiment concerns a mono-sheet material, which is processed as in the case of two separate sheet materials, and therefore occupies an intermediate position between the two aforesaid systems.

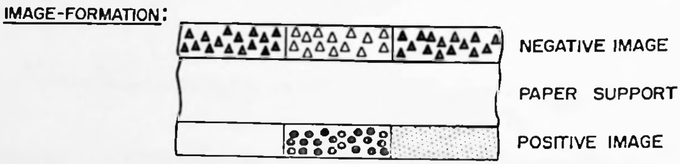

Fig. 5.10. Image formation in double-sided material.

Another method provides for a transparent support to be coated in succession with an image-receiving layer, a layer containing a white pigment and a silver chloride emulsion. Thus the two active layers are separated by an opaque white layer, which does not interfere with the diffusion transfer process, but

which separates the negative and the positive image efficiently. Two variants of this system are described in the patent literature.

First variant (Eastman Kodak Company, Ilford Ltd.—Figures 5.11, 5.12).[26,27]

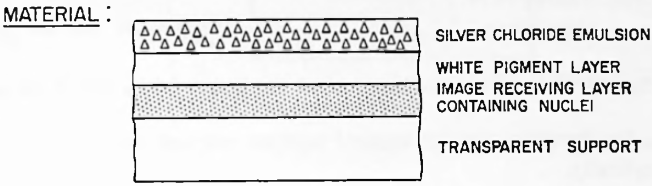

Fig. 5.11. Material with two active layers separated by white opaque layer.

Exposure: By print-through contact with an original printed on one side.

Processing: Development and transfer in a bath containing sodium thiosulphate.

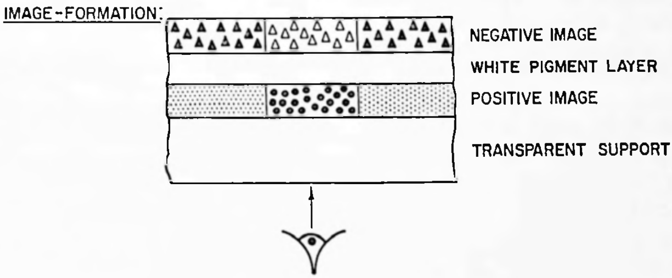

Fig. 5.12. Image formation in material with two separated layers.

Remark: The copy must be viewed from the transparent back.

Disadvantage: The presence of an obtrusive negative image under the positive image.

Gevaert-Agfa NV[29] describe a material of this type, in which the negative layer, however, does not intrude. For this purpose a special emulsion which shows a very low covering power after development, was elaborated. This improvement promises well for the future of this system.

Second variant: (Eastman Kodak Company, Fuji Film Co.).[26,28]

As in the first variant, the two active layers are separated by a white pigment layer. In this case, however, the order of the layer is reversed (Figures 5.13, 5.14).

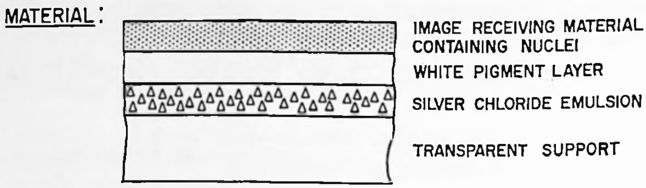

Fig. 5.13. Variant of separated layer materials with image-receiving layer on top.

Exposure: By print-through contact with an original printed on one side, or optically.

Processing: Development and transfer in a bath containing sodium thiosulphate.

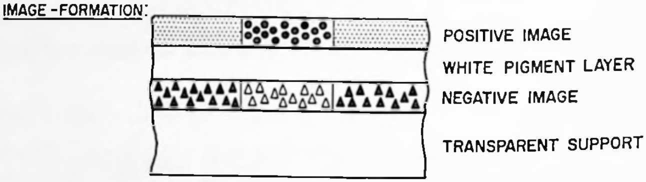

Fig. 5.14. Image formation in separated layer material with positive image on top.

It should be noted here, that, after processing, the negative image remains visible on the back. The effect of this may be disturbing.

According to another method, the material consists of a paper support, a silver halide emulsion, a layer containing a white pigment, and an image-receiving layer containing nuclei.[30–35] The composition of the white pigment layer should be such that it is able to transmit actinic light. The negative image is not obtrusive, since it is enclosed between the pigment layer and the paper support (Figures 5.15, 5.16).

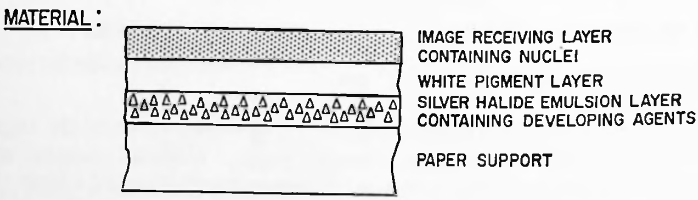

Fig. 5.15. Variant of separated layer material with developing agents in emulsion layer.

Exposure: Optical exposure with a mirror or by print-through contact with an original printed on one side.

Processing: Development and transfer in a bath containing sodium thiosulphate.

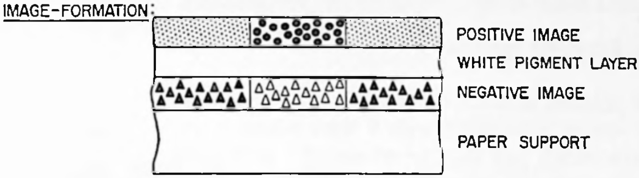

Fig. 5.16. Image formation in separated layer material with developing agents in emulsion layer.

Gevaert-Agfa NV[36] have filed a patent application for a process, in which a highly-sensitive material provided with a white pigment layer and nuclei, is exposed by reflected light and is subsequently passed through an activator solution, and finally fed between two rollers. The processing can be carried out manually or in a dark-room or fully automatically in a special processing apparatus.

A material of analogous composition but characterized by a lower sensitivity, is suitable for making contact exposures through the back of an original printed on one side (print-through contact). The latter material can be processed in subdued daylight in any commercially available copying and processing apparatus which is suitable for the silver complex DTR process.

The pigment is an important component of these materials. It must however fulfil certain conditions. It should allow the passage of the light during exposure as well as of the diffusing complex silver salts during processing. Moreover, it must be sufficiently white to mask the grey colour of the subjacent emulsion layer after processing, and thus enable the copies to acquire sufficient contrast. Colloidal titanium dioxide is very suitable for use as a white pigment. To fulfil all these conditions, the relative proportions of the binder and pigment must be carefully adjusted within the following limits:

pigment: 10 to 30 g/sq m
binder: 0·5 to 3 g/sq m

Beyond or below these limits optical difficulties are encountered either during exposure or after the image has formed. Since a reflex method is required for making the exposure, a highly sensitive emulsion has to be used: the emulsion may, however, contain a considerably smaller amount of silver than those which are intended for use in the process which employs separate negative and positive materials. The reason for this is that the whole process is carried out in situ and there is no transfer of silver to a second support. Moreover, practically no silver is lost. All the silver is used for forming the image. Even at relatively low concentrations it gives good coverage during the secondary DTR

development. The material, if it contains the requisite developing agents, can be processed in an activator solution.

5.2 *Stencil printing systems*

Stencil printing is based on the following technique. A coarse porous membrane or screen is provided with a layer which is impervious to ink except in those areas which will later constitute the printing image areas. The stencil which is thus formed is brought into contact with the surface to be printed and a paste-like ink is applied to the stencil by means of a roller or blade (Figure 5.17). The ink passes through the openings in the stencil, and the image is printed on the paper.

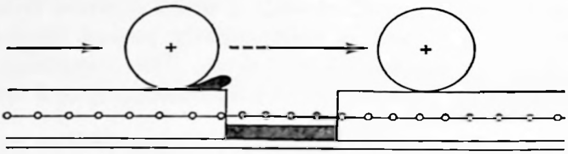

Fig. 5.17. Principle of stencil printing.

The almost naïve simplicity of this process explains its success in office work for duplicating texts, and the suppliers of some stencil duplicating machines have become renowned during the last fifty years.

The blank stencil commonly used consists of a thin porous paper—so-called Yoshino paper—also called Japan paper—(Figure 5.18) which has been rendered impervious to ink by the application of a wax-like substratum.

The text to be reproduced is typed on a stencil by means of a typewriter without a ribbon. The typewriter keys perforate the wax-layer thus making the sheet locally permeable to ink. The reproduction of drawings is a much more cumbersome procedure since a toothed roulette has to be used for recording. Thus, it is easy to understand why for a long time, attempts—which have met with varying degrees of success—have been made to prepare stencils by a photographic technique. Many different processes have appeared on the market which, although they give good results from the point of view of printing, can hardly be left in the hands of the average office employee since they require a high degree of technical skill.

A very reasonable and easy solution to this problem was offered by the preparation of stencils which embodied the concepts of the DTR-process. Only two treatments are involved in this process:

1. the image of the original to be reproduced is transferred by means of the DTR-technique to a special kind of positive material, on a Japan paper base.

2. the material bearing the image is subjected to a special after-treatment in which the silver image areas in the colloid layer of the material are selectively removed, thus exposing the Japan paper base in these areas. The resulting photographic stencil is ready for use.

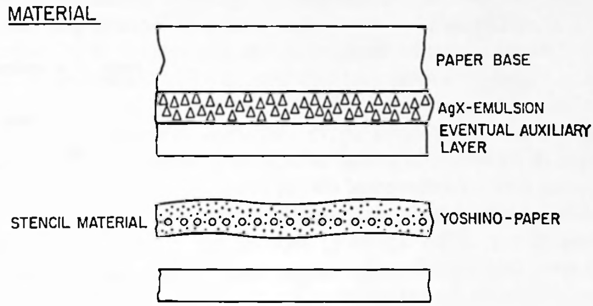

Fig. 5.18. Transferring the image of the original to special stencil material.

Exposure: reflex.

Processing: by means of a DTR-developer in an office copying apparatus, time of contact: 60–90 sec.

After-treatment: with hydrogen peroxide and copper salts (as described below. The stencil is then ready for printing.

The after-treatment is typical of this technique of preparing stencils. It is based on the etching, and disintegrating action of hydrogen peroxide and copper salts in an acid medium on the gelatin in the silver image areas.[37–40]

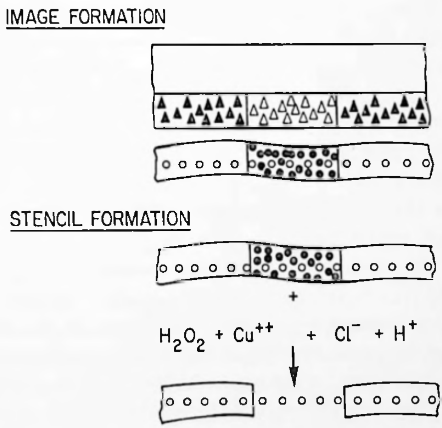

Fig. 5.19. Image formation and production of photographic stencil.

A typical formula for an after-treatment bath of this kind is as follows:

Solution A:	hydrogen peroxide (30% by volume)	100 ml
	water	900 ml
Solution B:	copper sulphate-5-water	110 g
	citric acid	150 g
	potassium bromide	8 g
	water to make	1000 ml

The after-treatment is carried out in two steps: the stencil is impregnated with solution A by means of a wad of cotton wool after which solution B is applied by means of a fresh wad of cotton wool.

From this moment onwards, etching commences: the dark silver image gradually becomes fainter. After about 15 seconds the image—and therefore also the colloid layer bearing the image disappears and the stencil is ready for use. Printing can start after the stencil has been dried by means of the same wad of cotton wool. The hydrogen peroxide and copper sulphate solutions can obviously be used in one bath. This mixture is however unstable so that when it is not used continuously, it is preferable to use separate solutions.

The entire reaction etching between image silver, binder and hydrogen peroxide, is not yet fully understood. The action is probably based on the phenomenon of heterogeneous catalysis in which the presence of metallic silver plays a prominent part.

5.2.1 REMARKS ON THE PROCESS. The negative is analogous to that used for office copying; however, its composition can influence the print quality considerably.

In fact, when the negative material employed simply consists of paper with a layer of silver halide emulsion which has been hardened in the usual way, the structure of the Yoshino-paper is such that it can easily give rise to the inclusion of air bubbles or cavities filled with liquid developer. The result is that the silver is transferred heterogeneously in such a way that it becomes concentrated mainly on the fibres and the entire image is discontinuous: thus the material has a poor resolving power.

However, when the negative is provided with an after-layer consisting of a hydrophilic colloid, which has been either slightly hardened or not at all, the image quality of the stencil is considerably improved.[41] It appears that the hydrophilic colloid is softened by the developer thus enabling intimate contact to be established between the negative and the receiving layer of the stencil: the silver is transferred homogeneously and the quality of the image is improved. Moreover, the transfer ratio, i.e. the ratio of silver deposited in the receiving layer to the amount of silver originally available in the negative appears to increase considerably, thus giving greater latitude when the image areas are etched.

In manufacturing stencils it is important to apply the gelatin in such a way that at the side which will come into contact with the printing stock, all the fibres of the Yoshino-paper are completely embedded in the gelatin. If any of the paper tissue remains uncovered the ink will be absorbed in the fibres at the edges of the image openings and the quality of the print will gradually deteriorate. It is possible to obtain stencils with particularly smooth and compact surfaces by first applying the gelatin to a smooth support, setting the gelatin layer and, while still wet, calendering the Yoshino-paper in the gelatin layer. The surface of the smooth support must be such that no permanent anchorage of the gelatin layer to this support takes place. After drying, the stencil can be removed from the temporary support by stripping.[42]

The gelatin layer which functions as the image-receiving layer contains development nuclei as well as coating aids and hardening agents. The intensity of the ultimate positive silver image depends on the amount of gelatin per unit area as well as on the degree of hardening. In fact, the catalytic disintegration of the gelatin by the copper salt and the hydrogen peroxide solution cannot take place unless the ratio of silver to gelatin exceeds a certain minimum value. On the other hand, too great a degree of hardening will restrain or even prevent the gelatin from disintegrating in the image areas, whereas insufficient hardening will cause the gelatin to swell too much and thus make it very liable to become damaged.

For the sake of completeness it should be mentioned that other systems for obtaining a stencil master are conceivable. The positive layer containing the nuclei could consists of a thermoplastic material which would be given the requisite characteristics by selectively melting it by means of IR-radiation.[43,44] This would result in the formation of a so-called thermographic stencil,[45] but up to the present no means have been found for putting this idea into practice (A hydrophobic layer, which cannot contain nuclei, in contrast to a hydrophilic substrate).

The supporting sheet which may consist of a sheet of plastic, an impermeable paper, a thin metal foil or the like makes the otherwise rather flexible stencil material somewhat more rigid when it is introduced into the developer. Thus, it can be used as many times as desired. After the negative has been separated from the positive, the stencil remains in contact with the supporting sheet until the end of the after-treatment.

5.3 *Modified processes*

5.3.1. THE CARBORAPID-PROCESS.[46,47,48] This process, which is no longer available on the market, is based on the DTR-process and enables masters for spirit duplicating to be produced photographically. It therefore offers all the advantages of the ordinary DTR-copy as regards the reproduction of coloured originals, and particularly the reproduction of aniline colours.

As is already known, a positive, but laterally reversed, dye image is used as the master sheet for the production of copies in spirit duplicating machines. The duplicating paper which is brought into contact with this master sheet is first moistened with alcohol which softens the fine layer of the hectographic dye deposit thus making it transferable to the paper.

5.3.1.1. *Preparation of the master sheet.* For the preparation of a master sheet by means of the Carborapid process, a negative material such as is used in the ordinary DTR-process, as well as a positive material, which is in the form of a dye sheet, are required. The negative is exposed to the original by the reflex, contact or print-through contact method after which the two materials, with the emulsion layer of the negative facing the dye layer of the positive, are fed into a conventional diffusion transfer copying apparatus filled with a developer of the same composition as that used in the Copyrapid process. On passing between the two rollers in the apparatus, the surfaces of the two materials are brought into contact with each other and firmly squeezed together.

After being left in contact for about 1–2 min the negative is separated from the dye sheet whereupon dye is left adhering image-wise to the unexposed areas on the negative. A positive, laterally reversed dye relief image is obtained on the latter. The dye relief image is then ready for immediate use as the master sheet in a spirit duplicating machine.

Depending on the required printing intensity, which can be regulated by appropriate adjustment of the pressure and the degree of moistening in the spirit duplicator, approximately 100 copies of good image density or 200–300 of inferior density but nevertheless easily legible copies can be obtained from a master sheet of this kind.

Composition and functioning of the material are represented in Figure 5.20.

The composition of the negative emulsion layer is analogous to that of the Copyrapid negative material. It differs from the Copyrapid positive material, however, in that the development nuclei are not present in the dye layer, which serves as the positive layer, but in a very thin layer on top of the negative emulsion layer. The dye layer consists of a hectographic dye and a mixture of binding agents which are water-soluble and/or capable of swelling in water and alcohol, and, like the Copyrapid positive layer, it contains sodium thiosulphate as solvent for the silver halide.

While the two sheets, moistened with developer, are in close contact with each other after having left the developing apparatus, thiosulphate diffuses from the dye layer into the negative layer where it dissolves the silver halide in the unexposed image areas. This silver halide is reduced in the thin, highly active nuclei layer and in these areas, a very dense silver deposit forms.

Plate 5.1 shows electron-microscope reproductions of sections obtained in a Carborapid model experiment. In this experiment the positive layer did not

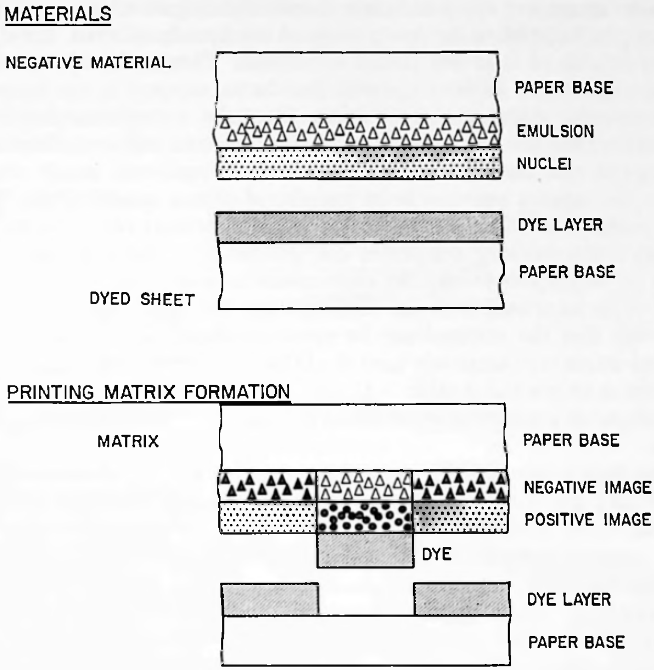

Fig. 5.20. Preparation of a master sheet by means of the Carborapid process.

contain any dye and the negative emulsion was coated on a baryta coated paper support.

The silver deposited on the surface of the negative adheres more strongly to the dye layer than to the other exposed areas on the surface of the negative in which there is no silver deposit and thus when the two sheets are separated only the dye is stripped out and transferred to the unexposed areas in the negative.

From electron-microscope observations it appears that, during development, the coarse-grained surface silver in the unexposed image areas of the negative diffuses into the porous dye layer in the positive so that when the two sheets are separated the dye layer, which is still soft, is stripped-out image-wise and left adhering to the negative.

If, in addition to the nuclei layer on the negative, development nuclei are also provided in the dye layer, the Carborapid process fails to work. In fact, the silver ions can only be reduced in the image areas in the nuclei layer but not in the dye layer.

In order to achieve sharp and clear detail-rendering in addition to sufficient processing latitude when the dye is stripped out and transferred, the dye layer must be capable of satisfying certain conditions. Firstly, the dye must adhere more strongly to the negative material than to the support in the image areas, but less strongly in the non-image areas. Secondly, notwithstanding its moist and swollen condition the cohesion of the layer should still be sufficient during stripping-out and transfer to enable it to be stripped-out neatly and right down to the support and thus to be transferred almost quantitatively.

It is evident that such a complicated transfer process can only take place efficiently if the working conditions are satisfactory. The dye layer must be capable of swelling to exactly the right extent to enable it to be stripped out sharply. The composition of the binder in the dye layer can be regulated in such a way that the material can be processed fairly well in the developing apparatus which are commonly used for DTR-materials and in which the bath is 8–12 cm in length and it takes 7–12 sec for an A4-paper sheet to pass through the developer at a temperature of 18–24°C and again with times of contact of 2–4 min.

The dye layer consists mainly of crystal violet dispersed in a mixture of binders (about 5–10 g per sq m), in addition to sodium thiosulphate (about 2·5 g per sq m) and some moistening agent. Most of the well-known water-soluble binding agents which are able to swell in water or alcohol are suitable for use in the dye layer; these include cellulose derivatives preferably carboxymethyl cellulose, starch derivatives, alginic acid esters and alginates, polyvinyl pyrrolidones and polyvinyl alcohols, polyvinyl acetates, polyethylene glycols, polysaccharides such as guar and carob bean flour products, dextrine, tragacanth and proteins such as gelatin and casein.[19]

Since the mixture of binding agents in the dye layer is of importance not only for stripping-out and transferring the dye layer but also for the printing process, the combination of binding agents should be adapted to the peculiar characteristics of this process. Binding agents which are decomposed or precipitated by alcohol may become horny in the master sheet, and when this happens the dye can no longer be dissolved away. Therefore, it is necessary for the dye-binder layer to be capable of swelling in the mixture of alcohol, water and glycerin which is commonly supplied with a spirit duplicator.

A silver chloride emulsion of the same sensitivity as that used in Copyrapid negative materials can also be used for the Carborapid negative material. However, in theory, all conventional emulsions of suitable steep gradation are suitable for the Carborapid process.

Heavy metals, their sulphides or selenides as well as organic compounds which passes nuclear activity and which are commonly employed in the DTR-process can be used as development nuclei since they do not influence the stability of the negative emulsion.

The developer can have a composition analogous to that used for the

Copyrapid process, with the difference however, that less sodium hydroxide and instead some tertiary phosphate is added in order to improve the swelling properties of the materials.

5.3.1.2 *Heat printing by the Carborapid process.* Although this process has already been demonstrated at exhibitions, it has never established itself in

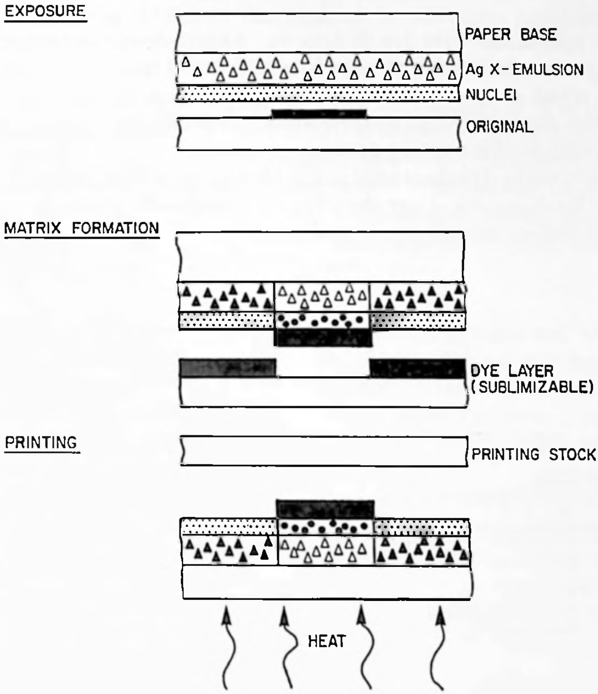

Fig. 5.21. Principles of heat printing by the Carborapid process.

practice. As its name implies, in this copying process a master or master sheet is produced in accordance with the Carborapid principle. Copies are made from this master by the application of heat.

The negative material and the developing solution are identical to those used in the production of the corresponding Carborapid material. The sole difference is that instead of a hectographic dye which is soluble in alcohol the dye sheet contains a sublimable dye, which has been emulsified in a suitable mixture of binding agents.

When a master of this kind is placed in contact with a sheet of ordinary

paper or a sheet of coated writing paper, and when heat is allowed to act on the sandwich through the rear of the master, e.g. by pressing it for a short time against a hot plate at about 120° to 160°C, a small quantity of the dye will sublimate and pass from the master to the receiving sheet and give a sharp copy. The colour intensity of the resulting prints depends on the intensity and duration of the heat treatment. Each master will give on an average of from 20 to 30 intensively dyed copies or 30 to 50 less strongly dyed but nevertheless quite legible copies.

Suitable sublimable dyes are as follows: Sudan dyes, Ceres dyes and dyes such as nigrosine, brilliant blue, para-blue and petrol blue (Benzin-blau).[51] The latter dye, which is an anthraquinine dye, is used in preference.

As in spirit duplicating, no suitable black sublimable dye has yet been found for this thermographic copying process.

In addition to the dye sheet used in the photographic manufacture of printing masters for heat-copying, a dye sheet for the mechanical production of thermographic duplicating masters has been developed; as in the case of hectographic

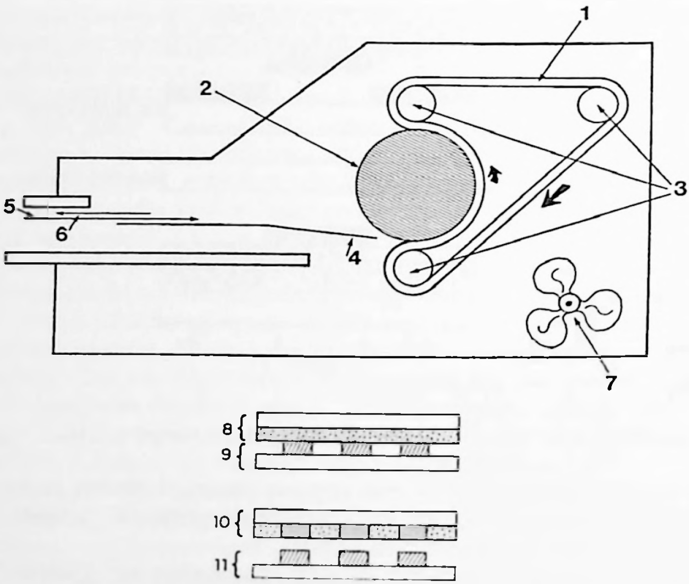

Fig. 5.22. Thermal duplicating machine. 1, siloprene belt; 2, heating roller; 3, tensioning and pressure rollers (for pressing the sandwiched materials into close contact together); 4, doctor blade (for separating the sandwich from the heating roller); 5, sandwich is introduced into the apparatus; 6, sandwich leaves the apparatus after duplicating; 7, propeller for cooling the motor; 8, 9, duplicating paper with coating of synthetic resin; 10, duplicating master; 11, thermographic print.

papers it is possible to write or type on this sheet.[52] It consists of a thin paper base, to which has been applied a layer of synthetic resin which can be transferred by pressure and which incorporates a sublimable dye, preferably petrol blue. Suitable synthetic resins are polycarbonates,[52] copolymers and graft polymers of acrylonitrile and styrene or of butadiene, acrylonitrile and/or styrene.[53] When the dye sheet is stripped out the edges are sharp and it is transferred practically quantitatively. It yields a sharp "erect" dyestuff relief.

From a duplicating master of this kind, up to 100 sharp prints of adequate colour intensity can be obtained.

5.3.1.3 *Apparatus for heat duplicating*. For duplicating, it is convenient to use apparatus which contain a roller which is heated to about 120–160°C and which is rotatedb y means of a heat-resistant belt of polytetrafluoroethylene or siloprene rubber, which in its turn passes over 2 rollers which ensure that the duplicating masters, receiving-paper and heating-roller remain in contact for a sufficient length of time. Figure 5.22 illustrates the essential features of a thermal-duplicating apparatus of this type.[54]

5.3.1.4 *Duplicating paper*. In theory any duplicating paper can be employed as the image-receiving paper, but it is preferable to use those with the smoothest surface since the surface condition of the paper is liable to influence the uniformity with which the sublimating dye is precipitated in such a way, that on rough paper surfaces, non-uniform, blurred copies are obtained. When, however, the receiving paper is coated with a thin layer of synthetic resin, e.g. polyvinyl acetate,[55] which softens at the temperature of the duplicating operation, and into which the sublimating dye penetrates and is able to distribute itself uniformly in the form of a solid solution, intensely coloured, uniform, and consequently sharper prints are obtained. At the same time, the print becomes scratch-proof and when stacked does not transfer any dye to the sheets lying on top of it.

5.4 *Aerial and Space photography, oscillography*

The fact that the DTR-system is able to deliver images which are available almost immediately has led to the design of certain modifications which—with the aid of adequate equipment—are always used when quick results or automatic processing are of the utmost importance.

When aerial photography is used for cartographic purposes it is often useful to be able to judge the results during the actual mission in order if necessary to take a fresh series of photographs. Rapid access to the required information is of great importance in the case of tactical reconnaissance flights. Automatic

processing is a valuable tool for telerecording certain parameters or for increasing the speed of data storage during unmanned space flights. Oscillography may be classed together with these special applications. In this field the scientist or technician has come to rely more and more on the means, which are peculiar to the photographic system of recording, of gaining rapid access to information.

Normally, the final aim of DTR-systems is to obtain a positive image. However high-quality negatives can also be obtained. It is obvious that in this case the DTR-systems present the only means of processing the exposed material rapidly and automatically. Both variants have their own specific applications.

The first step in the direction of rapid processing was already taken in 1913 when F. Hochstetter[56] applied for a patent in which he presented a solution —without resorting to conventional processing liquids—for processing the material in the camera itself with the aim of obtaining a good negative. A compact developing unit has to be designed (Figure 5.23) in order to obtain the desired effect.

The main part of such a developing unit consists of a strip of felt or other similar absorbent material saturated with a mixture of developing agent, sodium sulphite, water, glycerin, alkali carbonate, sodium thiosulphate and citric acid. The strip is wound on a spool which is placed in the camera in such a manner that the emulsion side of the exposed material is in contact with the strip. In this way, the development of the sensitive material starts immediately after exposure.

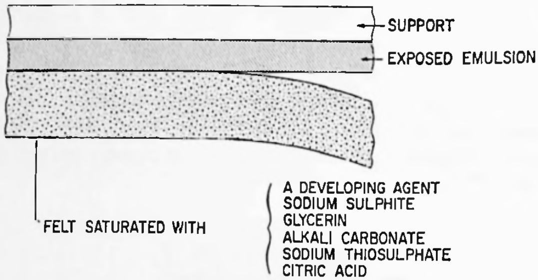

Fig. 5.23. Developing unit for processing film in the camera.

This procedure does not rely on AgX-diffusion transfer, as no developing nuclei are present. Moreover an AgX-diffusion-inhibiting action is set up by the high concentration of sodium thiosulphate in the strip. The developing mechanism may be compared with a developing-fixing process (one step process) as in the case of the so-called "monobath" systems.

Almost the same technique, but using a DTR-mechanism, is to be found

in a patent application[57] filed by E. Land in 1944. The subject of this specification is the production of a high-quality positive (Figure 5.24).

L. W. Tregillus *et al.*[58] in 1959 applied for a patent for a DTR-method of obtaining a good negative.

The technique consists of a one-step system for the rapid processing of a sensitized photographic material, in such a way that, after treatment, a substantially fully developed and fixed negative of good photographic quality is produced. The very short processing cycle does not claim to prevent the negative from undergoing any change during long term storage without further treatment, since this negative is intended for immediate viewing or for printing purposes. The processing itself consists in bringing into intimate contact the silver halide emulsion, containing the latent image, and a hydrophilic organic

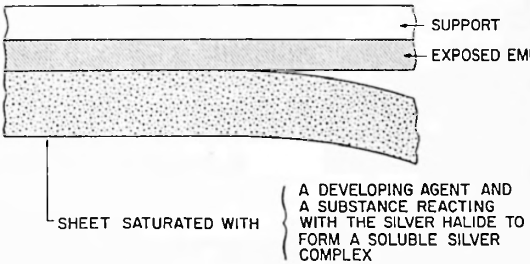

Fig. 5.24. Developing unit to produce a positive by the DTR process.

colloid processing web containing, besides a dispersed silver precipitating agent, sufficient processing solution to develop the exposed silver halide and to remove substantially all the undeveloped silver salt.

At the end of the above operation, the processing element is separated from the processed photosensitive layer which requires no further treatment of any kind. However, if the processed element is to be kept for archival purposes, it is advisable to wash it for a short time in water or to treat it with a stabilizer.

The resulting photographic negative is of acceptable quality. The same patent specification, also includes a diagram of an elementary apparatus for putting the system into practice (Figure 5.25).

In operation, the processing web 14 is wound from spool 12 on to the processing spool 11. Tank 13 is filled with the processing solution 16. The processing web 14 is then wound from spool 11 on to spool 12 as shown in Figure 5.25(A). It passes over rollers—if provided—through the processing solution 16 in tank 13. The rate of travel is such that the web absorbs a predetermined amount of processing solution. This amount is sufficient to develop and fix the film. After the treatment, the direction of rotation of spools 11 and 12 is reversed and the web again passes on to spool 12. The end of the exposed film 15 is then

connected to the core of the processing spool 11 in such a way that the emulsion side of the film is in contact with the hydrophilic surface of the web. The soaked web is sufficiently tacky to keep the end of the film in contact with the web on the spool 11.

After contact between the film and the web has been established, spool 11 is rotated in the direction shown in Figure 5.25(B), the emulsion side of the film

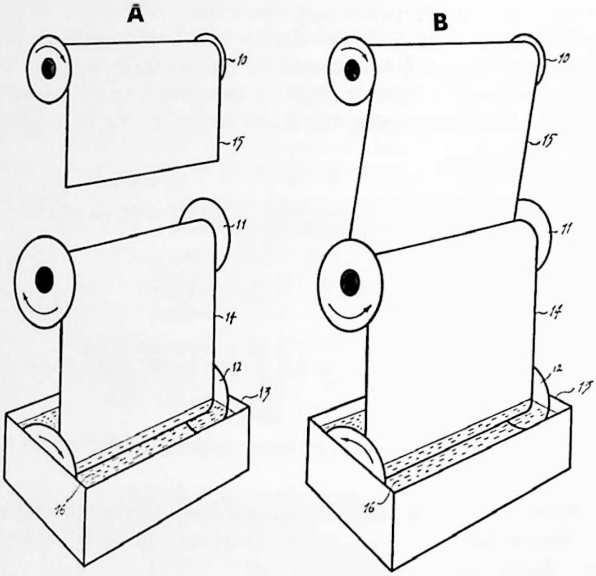

Figure 5.25. Elementary apparatus for rapid processing.

15 and the processing web 14 remaining in close contact until the film is substantially completely developed and fixed. At the end of the processing operation, the film and web are rewound on to their respective spools 10 and 12. In so doing, the web picks up fresh processing solution when it passes through the tank 13.

The patent application[50] filed by H. Yutzy *et al.* in 1961, presented a solution for improving the keeping properties of the processing elements. The stability of the processing elements left much to be desired owing to the presence of alkali-hydroxides by which the gelatin was strongly hydrolysed. H. Yutzy *et al.* proposed the use of a silver halide emulsion, which contains an alkali-releasing agent, which is developed by a processing element in which an inactive developer solution containing very little alkali is incorporated. This solution

consists of a developing agent and a very slightly soluble non-alkaline metal hydroxide.

The metal hydroxide and the alkali-releasing agent react to form a compound which dissociates less than the metal hydroxide. On the other hand a sufficient number of hydroxyl ions is produced to activate the developing agent and this results in the vigorous development of the exposed silver halide.

When, moreover, a silver nucleating or precipitating agent is incorporated in the processing element and the latter either contains a silver halide solvent or is soaked in a solution containing a silver halide solvent prior to use, the web may be designed in such a way that, not only a good negative is obtained in the photographic element, but also a good usable positive image is produced in the web.

During the Boston S.P.S.E. Meeting in May 1962, L. W. Tregillus presented a paper entitled "A diffusion transfer web process" which described a method for producing negative images with Kodak Special H.D. Aerial Film. The process was designed to process the material to its normal high standard of quality without human attention and irrespective of whether the processor was upside down or not. It was not the aim of the inventors to obtain usable positive images.

Further investigations of L. W. Tregillus and his colleagues resulted in a process which provided a positive image, and which could be used for processing other aerial films.

At the annual conference of the Society of Photographic Instrumentation Engineers, Los Angeles, August 1963, R. Tarkington presented a paper entitled "A new Kodak processing method for the aerospace age". In this paper, the name "Kodak Bimat Process" under which the system was placed on the market—was used for the first time to describe the diffusion transfer web process.

Figure 5.26 shows diagrammatically the different steps in the process. The processing film is soaked in a developing solution containing a silver halide solvent. This film is then brought into intimate contact with the exposed light-sensitive material. The developing solution in the processing film then diffuses towards the negative emulsion layer. The exposed grains develop and the unexposed ones dissolve in the silver halide solvent and move into the upper layer of the processing film containing silver reducing nuclei. In this way both a negative and a positive image are formed simultaneously.

Three different variations of this technique exist:

1. A simple wind-up process.
2. A continuous process using two processing films.
3. A continuous process using a single processing film.

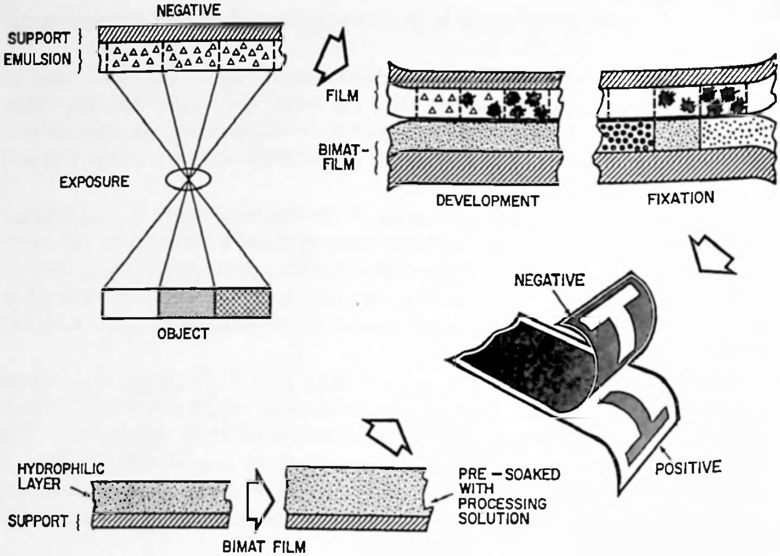

Fig. 5.26. Stages of the Kodak Bimat process.

5.4.1 THE WIND-UP PROCESS (Figure 5.26). The pre-soaked processing film is laminated to the exposed negative material by winding both together on to a single spool. They are kept in contact for a certain period, depending on the characteristics of the film. As the process comes to an end on its own accord

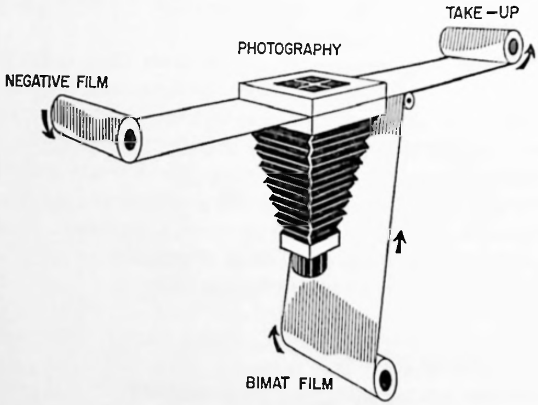

Fig. 5.27. Simple wind-up Bimat process.

(due either to the exhaustion of the developer and/or of the silver solvent or the lowering of the pH-value) the two materials can remain in contact for a considerable time before being separated. The only point that must not be neglected, is that they must not be allowed to dry while in contact with each other.

A very attractive feature of this mode of operation is that it enables the rates of transport of the film through the camera to be varied. Even the intermittent use of the latter is premissible, making the system most suitable for tactical reconaissance, since viewing during flight is not required. Moreover, a high quality positive and negative image are available as soon as the aircraft returns to its base.

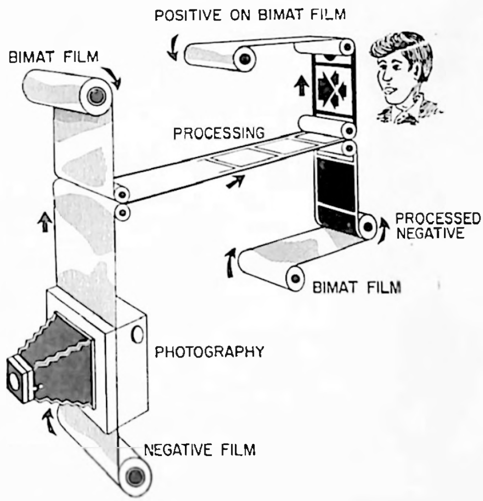

Fig. 5.28. Continuous Bimat process using two processing films.

5.4.2 THE CONTINUOUS PROCESS USING TWO PROCESSING FILMS (Figure 5.28). The first processing film is laminated to the exposed negative. The two materials are separated as soon as the positive image is formed. The negative is then immediately relaminated to a second strand of processing film. The second processing film and the negative material are kept in contact for a minimum time of 4 to 5 minutes. The two can then be separated or allowed to remain in contact until it is convenient to separate them. The processed negative material is then dried, after having, if necessary, been washed.

The great advantage of the process is the quick-access which it provides to a high-quality positive image.

However, the negative material also possesses excellent photographic characteristics.

5.4.3 THE CONTINUOUS PROCESS USING A SINGLE PROCESSING FILM (Figure 5.29). In this case, a pre-soaked processing film is laminated on to the exposed negative in a continuous processor. The two materials remain in contact until the processing is complete. They are then separated and allowed to dry, or protected, in some other way before being wound on to a spool.

The continuous processing system can also be adapted to provide a rapid access positive. Hence some systems in which the partially processed negative is discarded once the positive is available have been designed. The high-temperature, continuous processing method requires more critical control of

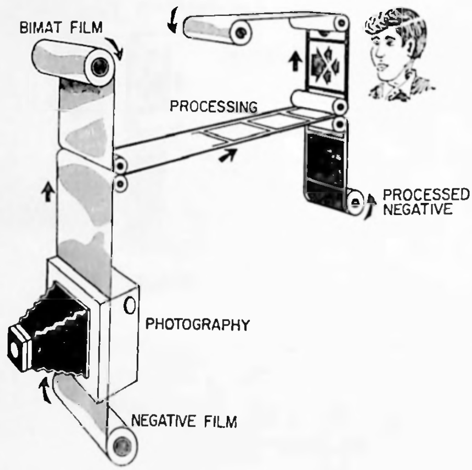

Fig. 5.29. Continuous Bimat process using one processing film.

temperature and lamination time than the other methods. It is best suited to those applications in which a monitoring function is required.

The photographic characteristics of the material as regards silver distribution, grain structure, sensitivity and information capacity were discussed in 1965 by L. W. Tregillus at the London Symposium on Processing Technology, and described in the Journal of Photographic Science.[60]

The materials and processes described are chiefly designed for and can be adapted to aerial reconnaissance and cathode-ray tube recording. In-flight processing is easily accomplished without free solutions being involved. When the simple winding-up process is used, processing can be completed and a positive image made available for immediate interpretation during the time taken for the aircraft to return to its base.

A complete line of processors, pre-soaking tanks and accessories for the

diffusion transfer web process has been built by Mark Systems Inc., of Santa Clara, California.[61] The Fairchild Hiller Corporation of Rockville, Maryland has worked out a mobile flight line processing system using the simple wind-up process.[62]

Aircraft of larger size can accommodate apparatus for the dual Bimat Transfer film method in which the positive is made almost immediately available for on-the-spot interpretation. This permits a quick examination to be made of the positive in order to determine whether the required information

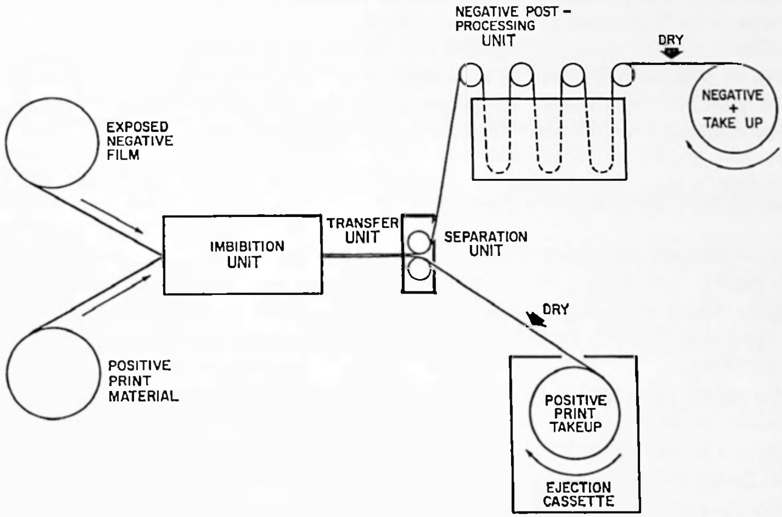

Fig. 5.30. Principle of the Ditrecon technique, using dry materials that are not moistened until they are brought together in the processor.

has been successfully recorded. If this is not the case, more photographs can be taken while the aircraft is still over the target area. Equipment for this process has been designed by the Eastman Kodak Company under USAF contract.[63]

The continuous processing method which gives rapid access to a positive image is also very suitable for cathode-ray tube recording. Two systems are at present available. In the first one a positive image is obtained very quickly, whilst the partially processed negative is discarded. In the second process, both a negative and a positive image are formed, but not as quickly as in the first system.

The Missile and Surface Radar Division of RCA, Moorestown, New Jersey, has designed equipment for the continuous method of Bimat Transfer processing which gives rapid access to the positive image.[64] This system was used during experiments with moonshots taken in the Ranger-programme.

The Fluidless Processor of the Nimbus Weather Satellite ground station equipment at NASA's Goddard Space Flight Center was built by Photo-mechanisms Inc.[65]

H.R.B. Singer Inc.[66] have built a complete line of mobile processors, even airborne, permitting both negative and positive images to be obtained by means of standard reconnaissance films in military logistics. This technique (Figure 5.30) uses dry positive and dry negative materials. The moistening of the film does not take place until the actual moment at which they are brought together in the processor. This method permits a practically indefinite alert status in an "operational-ready" condition.

The partially processed negative can be used for additional exposure when data or grid overlays have to be added. Further processing of the material is also possible. The Singer technique is known under the name of Ditrecon (which stands for Diffusion Transfer for Reconnaissance).

5.5 *Materials for X-ray DTR processes*

Conventional radiography has for a long time failed in one important respect. No matter how imperative it may have been to have rapid access to radio-graphs which were urgently required, say for making quick diagnoses, e.g. in operating theatres or infirmaries, such radiographs were not immediately forthcoming.

To satisfy this need it was necessary to develop a process which would, if possible, make the radiologist independent of the darkroom and which would shorten the photographic process to such an extent that the image could be examined almost immediately after it had been recorded. Since one of the most useful properties of the DTR-system is rapid access, a means of applying it to X-ray recording was sought.

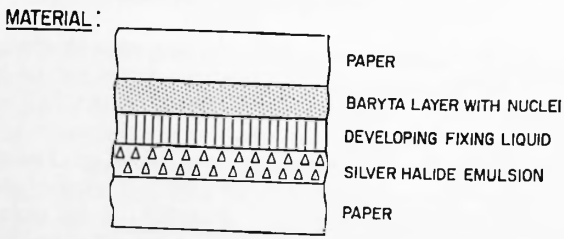

Fig. 5.31. Construction of material with pressure-sensitive layer of developing-fixing liquid between negative and positive layers.

Exposure: X-ray recording in cassettes.

Processing: the negative and the positive material are pressed into contact with each other.

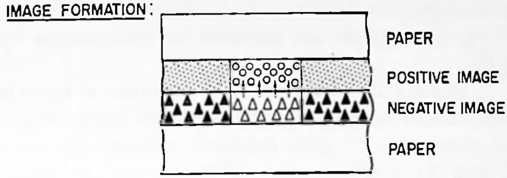

Fig. 5.32. Formation of negative and positive images after rupture of developing-fixing liquid container.

E. H. Land of the Polaroid Corporation did pioneering work in this field and, as early as 1947, he patented a process in which a photographic material was exposed image-wise and then pressed into contact with an image-receiving layer on baryta paper. The baryta layer had to be pre-treated with lead acetate, sodium sulphide and a mixture of lead acetate, cadmium acetate and zinc nitrate. Between the negative and the positive material there was a pressure-sensitive container with a developing-fixing solution. On exposure, the material was compressed so that the receptacle was ruptured. A positive image was created in the receiving layer, whereas a negative image was formed in the photographic material.[67] According to a special embodiment for dental radiographic film[68] the development was started by rupturing the container with the fingers or with the teeth, or by pressing it with the tongue against the palate after preheating it in the mouth.

In 1951 the system was improved[69] by making it possible to charge the X-ray cassette in daylight.

A patent was granted in 1955 to E. I. Dupont de Nemours[70] covering a photographic material in which an intensifying screen was placed between the support and the photographic emulsion. This intensifying screen consisted of a fluorescent pigment such as barium sulphate, lead sulphate, calcium tungstate or of other substances, e.g. zinc sulphide, which fluoresce on exposure to X-rays.

In 1961, Polaroid Corporation[71] proposed a sheet process according to which a material which also incorporated an intensifying screen was used. The composition of this material was as follows (Figure 5.33).

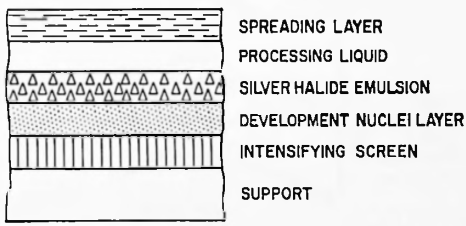

Fig. 5.33. Construction of Polaroid X-ray material with intensifying screen.

It was found possible to provide a stripping layer between the image-receiving layer and the photographic emulsion to facilitate the separation of the two layers. The X-ray photograph was intended for examination by reflected or transmitted light.

In 1962 E. I. Dupont de Nemours Co.[72] patented a material, of similar composition but without an intensifying screen. The image-receiving layer now incorporated a silver chlorobromide emulsion, whereas the actual light-sensitive layer consisted of a highly sensitive silver iodobromide emulsion.

In 1967 Gevaert-Agfa NV[73] patented a process for irradiating a light-sensitive material on a film support, developing it for 3 to 30 seconds in a processing liquid, the pH of which varied between 10·5 and 11·5 at a temperature of 25–35°C, and finally bringing the exposed material into contact with an image-receiving layer on a transparent film support at a temperature of 30 to 60°C.

The special characteristics of the last-mentioned process are:

A. Its very high sensitivity which is due to:

1. the fact that the DTR-system is less liable to fogging
2. the fact that the DTR-image (positive) is formed using the lowest part of the characteristic negative curve (see also Figure 5.33).

This high sensitivity can be enhanced considerably by the use of special techniques, for instance by increasing the time and temperature of processing (see Figure 5.34).

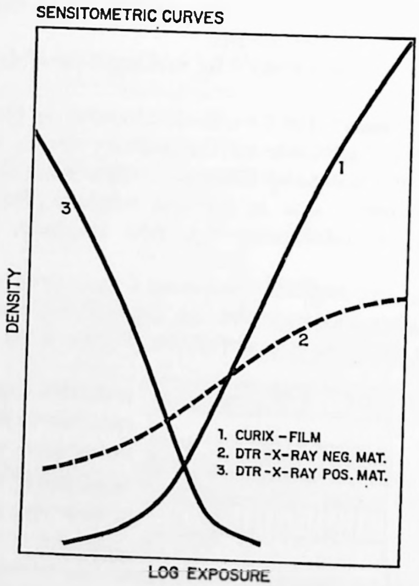

Fig. 5.34. Comparison of sensitometric curves of various X-ray materials.

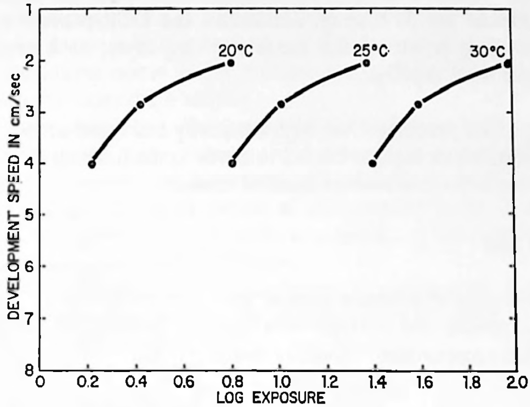

Fig. 5.35. Effect on sensitivity of variations in time and temperature of processing.

It is common knowledge that such a procedure gives rise not only to a more intense development of the negative, but also to a loss in gradation. Nevertheless by proper adjustment of the processing time, the desired positive gradation can be obtained with the same exposed negative. The softest gradation can in fact be obtained with a short time of processing in which the primary development is restricted. The steepest gradation requires slower development in which the pre-development is stronger.

Since the sensitivity of a material is increased much more by raising the temperature of processing than by prolonging it, it was obvious that the time of processing chosen should be such as would guarantee the optimum gradation, and the increase in temperature such as would secure the maximum gain in sensitivity.

In Table 5.1 the sensitivity of the DTR-X-ray material is compared with that of Curix-film.

TABLE 5.1

	kV	*mA*	*time(s)*	*mAs*	*Distance*
Curix-film	75	100	1	100	1 meter
DTR-X-ray material	75	100	0,3	30	1 meter

B. A low silver content.

C. Rapid Access.

Rapid access is influenced by different variables, the most important of which are:

(*a*) processing at a higher temperature, which leads to an acceleration in development. Moreover an increase in temperature when the negative and the positive materials are in contact, accelerates the DTR-process considerably,

(*b*) low swelling power of the image-receiving layer, as a result of which the copy dries more rapidly.

These important properties, viz. high sensitivity and rapid access, in combination with effective automation has led to a new system, which may certainly be regarded as an important asset in medical science.

5.6 *Contour film*

The phenomenon of diffusion transfer also occurs in combination with other photographic effects. An example of a material showing such characteristics is the so-called contour-film. Basically this material is built up as follows:

emulsion layer B
emulsion layer A + nuclei
film support

The emulsion layer A contains nuclei as well as hardening agents, whereas emulsion layer B remains unhardened.

A very alkaline ($pH > 13$) high contrast developer containing sodium thiosulphate is used in combination with this material.

After an image-wise exposure, the exposed areas both in A and B carry a latent image. After development, A will carry a primary image. In the unexposed areas the DTR-development of a secondary image will take place. As however the inhibiting effect of the products of reaction extends a little beyond the margins of the exposed areas—a phenomenon which is known as the adjacency effect—the primary and secondary images will be separated by a transparent line.

After development, the film is fixed and the emulsion layer B is finally washed off in hot water.

Thus, exposure through a negative transparency will give a transparent outline or "contour" of the original pattern.

5.6.1 MECHANISM OF CONTOUR LINE FORMATION. In the original publication[74] the formation of contours was explained in terms of the Sabattier-effect. Since then it was found that the presence of sodium thiosulphate in the developer enhanced the Sabattier-effect: the absence of developer agitation also tends to increase the effect (Miller-effect).[75,76]

Both these effects have been studied in single layer emulsions.

In comparison with the single layer systems, the "contour" film is characterized by having more transparent outlines surrounded by areas of high density. This can be understood if it be considered that the secondary image is created by the DTR-development which can be considerably retarded or completely inhibited by an increase of the Br^--concentration and of the oxidized developing agents and by a decrease both of pH and of the quantity of developing agents.

All these variations occur in the primary image and extend their influence by diffusion to the immediate vicinity.

In single layer emulsions the supernatant developing bath smooths out these local differences in concentration at a rate which is proportional to the agitation. In the contour film however, such a levelling out of the variations which are caused by the development of the primary image in A is largely prevented by the emulsion layer B, since in a swollen gel the transport of ions in both directions is governed by diffusion.

Moreover, the development of the primary image in layer B itself causes variations in the same direction and boosts the adjacency effect.

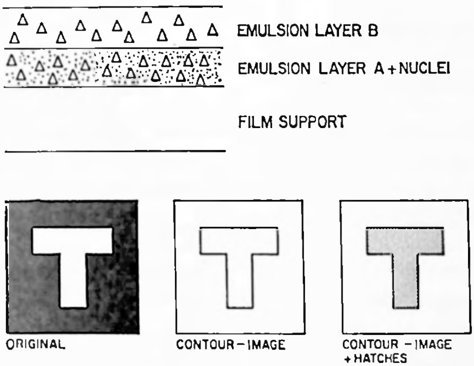

Fig. 5.36. Construction of contour film and mechanism of contour line formation.

In a publication on monobath developers, it was also suggested that a developing primary image can act in the capacity of nuclei for the reduction of dissolved silver salts, and therefore a considerable decrease in the concentration of the dissolved silver salts may be expected in the neighbourhood of the primary image.[77]

5.6.2 APPLICATIONS OF THE CONTOUR FILM. A very promising application of contour film appeared to be in the field of textile printing, in which contour images are frequently used. For this purpose, the screen lines required for textile printing, the so-called hatches, had to be introduced into the areas demarcated by the contour lines.

This is made possible by sensitizing orthochromatically the emulsion layer B, whilst the emulsion layer A remains blue-sensitive. An image-wise exposure with *green* light only affects emulsion B, in which an image is formed after development; the products of reaction prevent development from taking place in emulsion layer A.

In the unexposed areas, the silver salts in both layers A and B are dissolved and yield a silver image on the nuclei which are present in A. After fixing and washing off layer B, a positive duplicate of the original is obtained.

An image-wise exposure with *white* or *blue* light will affect both emulsion layers and finally a "contour" image is obtained, as explained on the previous page.

In practice the procedure is as follows:

exposure in contact with the original negative
exposure, with green light, in contact with a line screen.

In this way a latent image of the screen is formed only in the upper layer.

developing in a bath containing sodium thiosulphate
fixing
elimination of the upper emulsion layer by washing it off with hot water.

Figure 5.36 shows the resulting image, which can be transferred to and etched out on a copper printing cylinder.

The width of a contour line can also be altered by varying the time of exposure, or by inserting transparent foils during the exposure. A large number of variations in the reproduction of an original are also possible.

In spite of the interesting properties of the material and its initial success, it was not generally accepted by the printing industry, for which it was intended. This can most likely be accounted for by the fact that in the late forties no dimensionally-stable supports were marketed and therefore in colour work, because of the hot water treatment, difficulties arose in getting the colour separation images into register.

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VI. THEORETICAL PRINCIPLES

It appears from the qualitive description of the processes given in chapter 2, that the process of silver complex diffusion transfer reversal comprises several physicochemical processes.

The exposed silver halide in the negative layer must be developed very rapidly in view of the consumption of silver halide in the exposed image areas. Thereupon the silver halide in the unexposed areas must be dissolved to form silver complexes which must be transported by diffusion to the positive layer, in which, by physical development, the silver ions are deposited from the complex solution on to development nuclei in the positive layer. The object is to obtain a neutral black image of the greatest possible covering power.

Therefore in this chapter the chemical and physical development (6.1) as well as the solution of the silver halide and the formation of complex compounds (6.2) and (6.1) will be discussed. Together with the processes of transport, the combined action of these single processes regulates the kinetics of the process as a whole (6.4). The properties of the silver deposited in the positive are dealt with in 6.9.

6.1 *The mechanism of photographic development*[1–7]

In photographic development the silver ions originating from the silver halide are reduced to silver by a reducing agent, the so-called developing agent. In photography it is of general and fundamental importance for the reduction of silver ions on metallic nuclei to take place several orders of magnitude more rapidly than in the absence of such nuclei. In this respect it does not matter whether, during development, these nuclei are in contact with the silver halide or not (see the chapter on chemical and physical development).

If, e.g., a silver halide emulsion layer is exposed image-wise, a so-called latent image is formed in it. By the absorption of light quanta, some of the silver ions in an exposed silver halide grain are transformed into silver atoms. These few silver atoms, which act as latent image nuclei, can then initiate catalytically the reduction of all the remaining (10^5 to 10^9) silver ions in the silver halide grain in question. In this way, by development, an intensification factor of 10^5 to 10^9 can be achieved.

On the other hand, in the silver halide grains which remained unexposed, the reaction of development is inhibited kinetically, because the activation energy necessary for the formation of the new phase (silver) must first be available there before the reduction of the entire silver halide grain can take place.

Photographic development is an electrochemical process. The active force in this process is the electrochemical potential difference between the redox potential E_{redox} of the developing agent and the Ag^+/Ag-potential $E_{Ag^+/Ag}$ of the developing solution under specified conditions (temperature, pH, pAg, and so on). In order to reduce the silver ions, the redox potential E_{redox} of the developing agent under the specified conditions for the developing solution must be more negative than the Ag^+/Ag-potential; on the other hand, the potential difference must not exceed a maximum value ($E_{Ag^+/Ag} - E_{redox} \leqslant 0{\cdot}3$ volt), as otherwise the probability of the spontaneous formation of silver nuclei (i.e. fogging) in such strong reducing agents becomes too great. During development the metallic nucleus acts as an electrochemical centre for the reaction; the molecules or ions of the developing agent migrate by diffusion towards the nucleus, supply electrons to this nucleus and thus become oxidized (anodic partial process). Simultaneously, silver ions migrate towards the nucleus where they take up electrons and are thereby reduced (cathodic partial process). The combination of anodic and cathodic partial processes can be elucidated by reasoning on the following line:

If a metallic silver nucleus is first present in a medium which contains mobile silver ions but no redox system, it will at first acquire the electrochemical Ag^+/Ag-potential $E_{Ag^+/Ag}$ of this medium, which depends only on the concentration of free silver ions. Between a nucleus and its environment there is then no electrochemical potential difference, and therefore no current of silver ions will flow from the environment towards the nucleus.

A current of silver ions i_{Ag} will not start to flow towards the nucleus, until an electrochemical potential E_n is imposed on the latter, which is more negative than the afore-mentioned Ag^+/Ag-potential $E_{Ag^+/Ag}$. With increase in the potential difference $E_{Ag^+/Ag} - E_n$ the current of silver ions i_{Ag^+} will generally increase. The relations between this silver ion current strength $i_{Ag}{}^+$ and the potential difference $E_{Ag^+/Ag} - E_n$ is termed the current voltage curve of the cathodic partial processes (Figure 6.1). The slope of this curve is governed by the electrical resistance, which restrains the current of silver ions.

This model conception is of absolutely general application, and it is completely immaterial, whether the mobile silver ions migrate in the solute phase as free or as complex silver ions, or are transported in the silver halide lattice in the form of Frenkel-defects.

If, on the other hand, the nucleus first comes into contact with another medium, which contains only a (developing) redox system and no mobile silver ions, the nucleus will at first acquire the electrochemical potential E_{redox} of this redox system. An electronic current i_e begins to flow towards the nucleus in form of (reduced) developer molecules as soon as an electrochemical potential E_n is imposed on the nuclei. This potential is more positive than the redox potential E_{redox} of the developer-redox system under the given conditions. In general the strength of this electron current i_E also increases with increase

in the potential difference $E_n - E_{redox}$. The relation between these two quantities is termed the current voltage curve of the anodic partial process (Figure 6.1). Anyhow, in the anodic partial process, the electron current (diffusion of the reduced developer agent towards the nucleus) is coupled with a diffusion of the developer oxidation product away from the surface of the nucleus on which it has been formed. Therefore, the slope of the anodic current potential curve in the diagram outlined in Figure 6.1 depends on the electrical resistance which

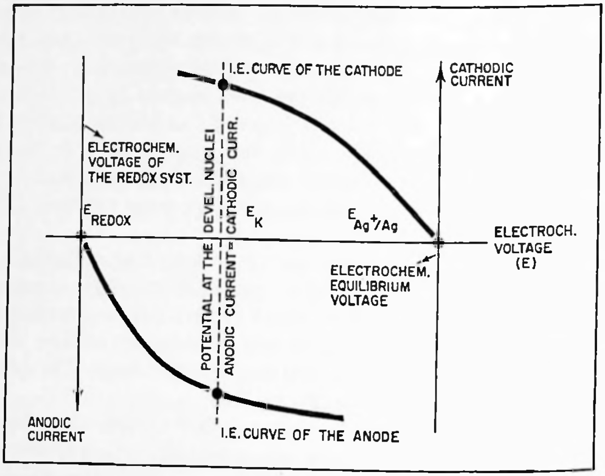


Fig. 6.1 Diagrammatic representation of the co-operation of anodic and cathodic partial processes in the total development process. Taken from R. Matejec and R. Jeyer, *Z. wiss. Photogr.*, 57 (1963), 18.

is set up in opposition to both these diffusion processes by the environment of the nucleus.

If now mobile silver ions as well as a (developer) redox system are present in the medium surrounding the nucleus, a silver-ion current as well as an electron current will flow simultaneously towards the nucleus. A stationary mixed potential E_n and a stationary development current i are established on the nucleus as soon as the strengths of the cathodic (i_{Ag^+}) and the anodic (i_e) currents becamc equal to each other:

$$i_{Ag^+} = i_e = i \tag{1}$$

As a result, the stationary strength of the development current i, which, according to equation (2), corresponds to the rate of growth of the silver nucleus:

$$i = e \, . \frac{dn}{dt} \tag{2}$$

is obtained from the point of intersection of the anodic and cathodic current voltage curves, if, instead of plotting, as in Figure 6.1, the current strengths of one or other sign, their absolute values are plotted against the electro-chemical potential.

It is evident from Figure 6.1 that a development current i which enlarges the development nucleus only exists when the redox potential E_{redox} of the developing solution is more negative than the Ag^+/Ag-potential $E_{Ag^+/Ag}$. If on the other hand, the current flows in the opposite direction, the silver development nucleus will then be destroyed by oxidation of the silver to Ag^+ ions (corrosion processes).

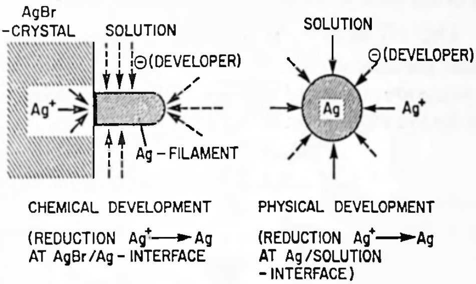


Fig. 6.2 Ideal mechanism of photographic development. Diagrammatic representation of chemical (left) and physical development (right).

In theory, photographic development can take place in accordance with two different types of mechanism:

If, during development, the development nucleus remains in contact with the silver halide grain and if the solution contains only a small quantity of (complex) dissolved silver ions, the anodic and the cathodic partial processes will take place at different phase boundaries: the transition of electrons from the developer to the silver nucleus takes place at the interface silver/solution; on the other hand, silver ions (in the form of Frenkel-defects) migrate through the silver halide crystal towards the nucleus and are reduced at the interface: silver/silver halide. In this way the silver grows out of the silver halide grain in the form of filaments. This type of development mechanism, which in diffusion transfer reversal can only occur in the negative layer, is termed chemical development (Figure 6.2, left-hand side).

If, however, there is no contact between the development nucleus and silver halide, but if the nucleus is completely surrounded by the solution phase during development, the (complex) dissolved silver ions as well as the electrons will be carried from all directions out of the solution phase towards the nucleus. During development the silver particle grows spherically. This type of development mechanism in diffusion-transfer-reversal occurs in the positive layer and has been termed physical development (cf. Figure 6.2, right side).

In Plate 6.1 two electron micrographs show, for comparison, filamentary silver particles formed by chemical development and spherical silver particles formed by physical development.

6.2 *Solubility products of silver halides*

In saturated solutions containing an excess of solid silver halide (AgX) in the form of a precipitate, an equilibrium is set up between the free silver ions (Ag^+) and the free halide ions (X^-) of the solution phase on the one hand and the lattice ions in the solid silver halide on the other hand:

$$(Ag^+, X^-)_{solid} \rightleftharpoons Ag^+_{(dissolved)} + X^-_{(dissolved)}$$

In consequence, the saturation concentrations $[Ag^+]_S$ and $[X^-]_S$ of free ions in the solution phase are controlled by the so-called "solubility products" S_{AgX}, which are given by the expression:

$$[Ag^+]_S . [X^-]_S = S_{AgX} \tag{1}$$

In aqueous solutions, the magnitude of the solubility products decreases in the order AgCl, AgBr and AgI; numerical values for different temperatures can be found from Figure 1. The temperature-dependence of the solubility products is determined by the heat of solution according to the equation:

$$S_{AgX} = S_{oAgX} \,.\, \exp\left[\frac{-\Delta H}{RT}\right] \tag{2}$$

where ΔH is the heat of solution, and S_{oAgX} is a factor of entropy of the solution process.

For AgCl, AgBr and AgI equation (2) has the following numerical values:

$$S_{AgCl} = 2{\cdot}10^{-\frac{3000}{T}} \tag{2a}$$

$$S_{AgBr} = 468{\cdot}10^{-\frac{4470}{T}} \tag{2b}$$

$$S_{AgI} = 33{\cdot}10^{-\frac{5090}{T}} \tag{2c}$$

The values of the heat of solution are therefore as follows:

$$\Delta H_{AgCl} = 13{\cdot}7 \text{ kcal/mole} \tag{3a}$$

$$\Delta H_{AgBr} = 20{\cdot}4 \text{ kcal/mole} \tag{3b}$$

$$\Delta H_{AgI} = 23{\cdot}3 \text{ kcal/mole} \tag{3c}$$

The temperature functions of the solubility products, given by the equations 2a, 2b and 2c are represented in Figure 6.3.

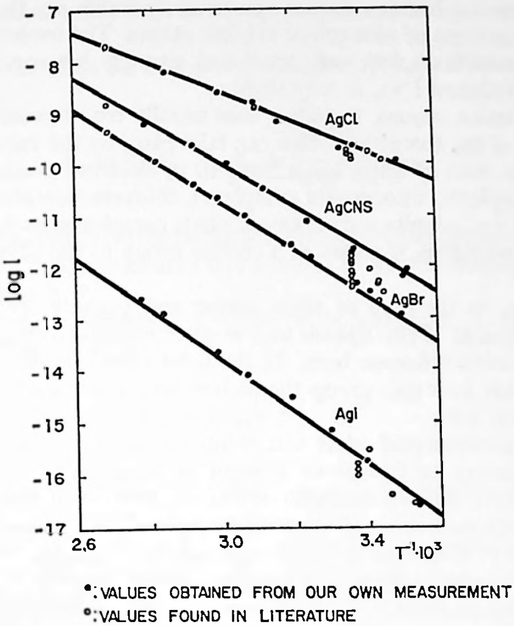


Fig. 6.3. Solubility products of silver halides in relation to temperature. Taken from: E. Klein, *Ergebn. der Wiss. photogr. Konf. Köln* (Reports of the Scientific Photographic Conference, Cologne, 1956). Pub: V. O. Helwich, Darmstadt (1958), 225.

6.3 *Complex compounds of silver ions*[8–13]

6.3.1 GENERAL CONSIDERATIONS. The poor solubility of some silver compounds in polar solvents, e.g. water, is due, to a relatively large extent, to the presence of homopolar bonds in these compounds. Therefore, in most cases, these sparingly soluble silver compounds can usually be converted into readily soluble complex silver compounds, simply by saturating these bonds. In other words, in most cases these sparingly soluble silver compounds are readily soluble in complexing agents. Consequently, silver complexes play an important part in photographic processes, especially in diffusion-transfer-reversal processes.

As typical ions of an element in an odd series, silver ions are capable of forming complexes with many substances. Because of the incompletely occupied 3d electron shell it is preferable to choose complexing agents which have free electron pairs available for the formation of covalent co-ordination bonds. The

silver co-ordination bonds which are particularly stable are those which form free pairs of electrons of nitrogen or sulphur atoms. The tendency of the silver ions to form complexes with very small and strongly heteropolar anions, e.g. fluoride and hydroxyl ions, is only slight.

As co-ordination centres, the silver ions usually tend towards a tetrahedral configuration of the complexes. This can take place by the successive addition of four ligands, each of which has a free pair of electrons available. Examples are halide complexes, thiocyanate complexes, thiourea complexes and others. In other cases, e.g. sulphite and the thiosulphate complexes, each of two ligands, in a state of saturation, is added as a chelate group to the silver ion with two electron pairs.

Nevertheless, in the case of silver amine and cyanide complexes, a rod-shaped arrangement of two ligands to one silver ion is known; hydration may possibly have some influence here. In the solid silver cyanide complex, however, the cyanide ions also group themselves into a tetrahedral configuration around the silver ions.

In strongly concentrated silver salt solutions, several silver ions (up to 8) can add themselves as ligands to a small multiple, negatively charged co-ordination centre. Known examples are silver complexes with anions of the fifth and the sixth even series (P^{-3}, As^{-3}, S^{-2}, Te^{-2}, and so on).

The tendency of silver ions to form complexes with certain special complexing agents is so great that in these complexes even higher oxidation levels of silver (Ag^{+2}, Ag^{+3}) become stable. In Ag^{+2} complexes four co-ordination bonds are always present in one plane.

6.3.2 THEORY. If, in accordance with the following reaction, a special ligand (R^{-p}):

$$Ag^{+} + R^{-p} \rightleftharpoons [AgR]^{-p+1} \tag{1}$$

$$[AgR]^{-p+1} + R^{-p} \rightleftharpoons [AgR_2]^{-2p+1} \tag{2}$$

$$[AgR_{(n-1)}]^{-(n-1)p+1} + R^{-p} \rightleftharpoons [AgR_n]^{-np+1} \tag{3}$$

is added to silver ions, then the following equilibrium conditions will apply to these complex equilibria (1)–(3):

$$\frac{([AgR]^{-p+1})}{(Ag^{+})(R^{-p})} = \beta_1 \tag{1a}$$

$$\frac{[AgR_2]^{-2p+1}}{([AgR]^{-p+1})(R^{-p})} = \beta_2 \tag{2a}$$

$$\frac{([AgR_n]^{-np+1})}{([AgR_{(n-1)}]^{-p(n-1)+1})(R^{-p})} = \beta n \tag{3a}$$

In these equations, the terms in brackets represent the respective concentrations.

The stability constant K_n of a given complex $(AgR_n)^{-np+1}$ is then given by the expression:

$$K_n = \beta_1 . \beta_2 \ldots \beta_n = \frac{([AgR_n]^{-np+1})}{(Ag^+).(R^{-p})^n} \tag{4}$$

which defines the relation between the equilibrium concentration of the complex $(AgR_n)^{-np+1}$, the concentration of free silver ions and the concentration of free complexing agents R^{-p}.

The dependence of the stability constants of complexes K_n on temperature is expressed by equation (5):

$$K_n = K_{n,o} . \exp \left[\frac{-\Delta H}{RT} \right] \tag{5}$$

In this equation $K_{n,o}$ is an entropy factor, which is independent of temperature, and ΔH is the enthalpy of complex formation.

In many photographic problems it is important to know the concentration up to which the different silver halides will dissolve in a complexing agent R^{-p} of a definite concentration. The required data can be derived from the solubility product

$$S_{AgX} = [Ag^+].[X^-] \tag{6}$$

of the silver halide AgX in question and from the stability constant of the complex which is formed in accordance with equation (4). The following relation between the concentration of the complex $([AgR_n]^{-np+1})$ and that of the free complexing agent R^{-p} is obtained

$$([AgR_n]^{-np+1}) = S_{AgX}^{\frac{1}{2}} . K_n^{\frac{1}{2}} . (R^{-p})^{n/2} \tag{7}$$

6.3.3 SILVER COMPLEXES OF SPECIAL PHOTOGRAPHIC IMPORTANCE. Of the large number of known silver complexes, only those of the greatest photographic importance will be discussed here.

The complex compounds which are formed from silver ions and thiosulphate ions are the most important silver complexes for the diffusion-transfer-reversal process, because in this process the silver ions are transported mainly in form of silver thiosulphate complexes.

The complexes which are formed from silver ions and excess halide ions greatly influence the solubility of the silver halides in photographic layers.

Sulphite is mostly present in developing solutions in order to prevent oxidation; and thus silver sulphite complexes form when a photographic layer is introduced into the developing solution.

The formation of the silver complex can often be accelerated by means of thiocyanate ions.

Amine complexes are of some importance in the manufacture of photographic emulsions.

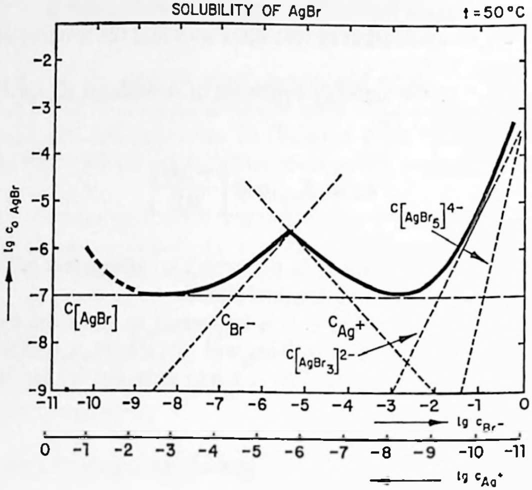


Fig. 6.4. Total solubility of AgBr at 50°C as a function of the concentrations of free $Ag^{+ +}$ ions and free Br^- ions (according to E. Klein and E. Moisae, *Z. Electrochem.*, **67** (1963), 349.

6.3.3.1 *Silver complexes with excess halide ions.* When aqueous solutions of silver salts are mixed with solutions of a halide, not only a sparingly soluble silver halide is formed, but considerable numbers of silver ions also are dissolved to form complex ions, especially if a large excess of halide ions is present. As an example, the solubility of silver bromide at 50°C has been plotted against the bromide concentration and against the silver ion concentration in Figure 6.4.

Near the point of equivalence ($c_{Ag^+} = c_{Br^-}$), which, e.g. can be recognized in Figure 6.1 by the solubility peak, practically only free Ag^+ ions and free Br^- ions are present in the solution. The solubility of silver bromide in this region corresponds practically entirely to the concentrations of the ions which are in the minority (c_{Ag^+} when Br^- is in excess; c_{Br^-} when Ag^+ is in excess) and which are still allowed by the solubility product. In this region these minority concentrations decrease with increasing excess of those which are in the majority.

When the excess of the latter is somewhat higher, both branches of the curve in Figure 1 descend to the horizontal line: below the concentration (c_{AgBr}) of the dissolved (Ag_1Br_1) in non-dissociated state, which is constant throughout the entire region of concentration, the solubility of silver bromide cannot decrease neither with excess of Ag^+ nor with excess of Br^-.

On the one hand, a very large excess of Br^- will lead to the formation of an $[AgBr_n]^{1-n}$ complex, whereas on the other hand, when Ag^+ is greatly in excess, an $[Ag_nBr]^{+n-1}$ complex will appear. The solubility of the silver bromide will then again increase rapidly with increasing excess of the ions which are in majority.

In regions where both the halide and the silver ions are in excess, a minimum will appear in the solubility curve (cf. Figure 6.4). The solubilities of the different silver halides in the region in which the halide ion is in excess have been plotted in Figure 6.5.

The mechanism of the combination of silver and halide ions to form complex ions is very simple: in the region of excess halide, halide ions are added successively to the silver ions with increasing halide concentration. In this way the halides of photographic importance (Cl^-, Br^-, I^-) pass through the complex series:

$$[AgX_1]^0; \qquad [AgX_2]^{-1}; \qquad [AgX_3]^{-2} \ldots [AgX_4]^{-3}$$

In the case of Br^- and I^- an additional complex $[AgX_5]^{-4}$ has been mentioned. The existence of regions of the different halide complexes is shown in Figure 6.3, whereas the stability constants of these complexes are listed in Table 6.1.

Aqueous solutions containing a large excess of silver ions, i.e. with small pAg values, are of little photographic interest. Therefore, we will not enter into any further discussion of the formation of $[Ag_nX]^{+n-1}$ complexes, which are formed in this region of concentration as indicated in Figure 6.4.

6.3.3.2 *Silver complexes with thiocyanate ions.* As in the case of halide ions, several thiocyanate ions are added successively to the silver ion with increasing thiocyanate concentration; thus the solubility of the silver thiocyanate also passes through a minimum with increasing thiocyanate ion concentration (see Figure 6.7).

Since, in the case of thiocyanate complexes, a complexing bond obviously is formed by a free electron pair of the sulphur atom, the bonds between the silver thiocyanate ions in the complex are fairly stable. On the other hand, equilibrium is established exceedingly rapidly, and thus the kinetics of the solution of silver halides by means of other complexing agents, e.g. sulphite ions, can often be accelerated catalytically by addition of thiocyanate ions.

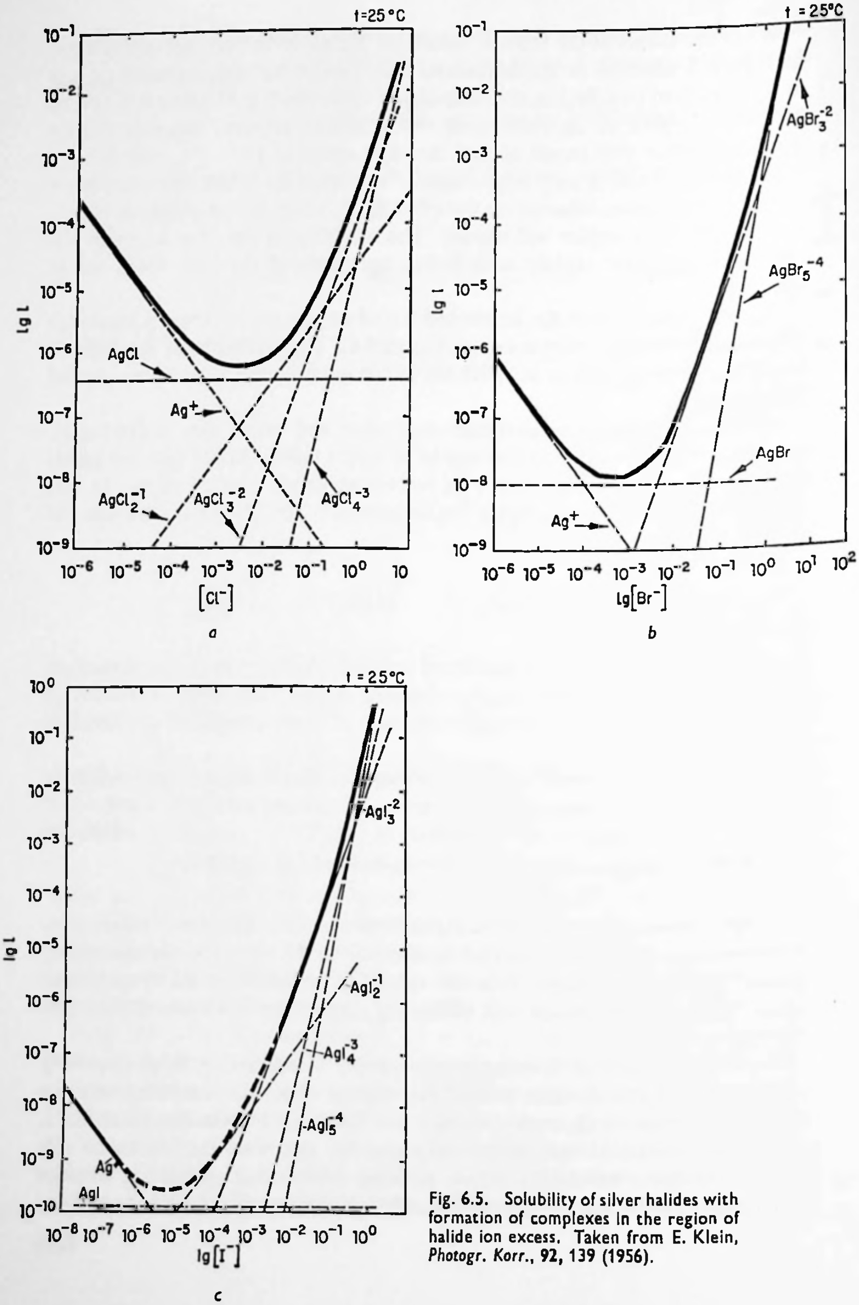


Fig. 6.5. Solubility of silver halides with formation of complexes in the region of halide ion excess. Taken from E. Klein, *Photogr. Korr.*, **92**, 139 (1956).

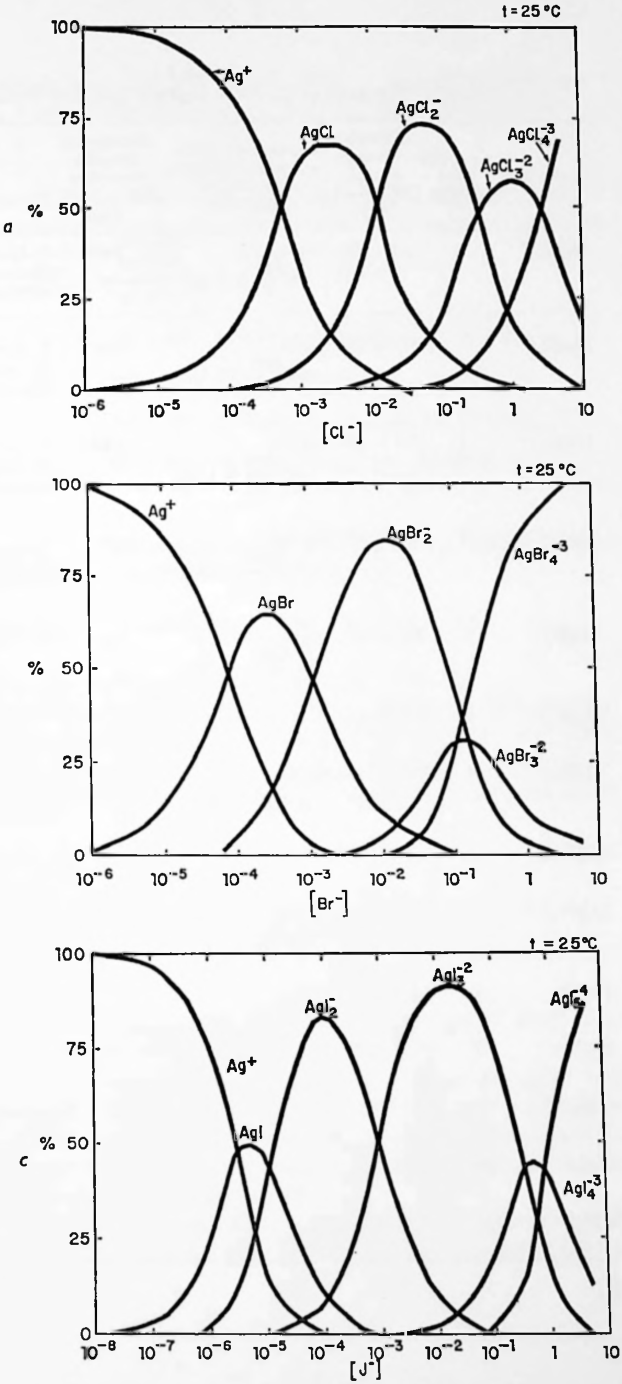


Fig. 6.6. Percentage participation of the various silver halide complexes in the total solubility of silver halides as a function of free halide concentration. Taken from E. Klein. *Photogr. Korr.*, **92**, 139 (1956).

TABLE 6.1

STABILITY CONSTANTS OF VARIOUS HALIDE COMPLEXES

Complexes	Co-ordination number	Stability constants of complexes at 25°C	Dependence of the complex stability constants on temperature	Enthalpy of complex formation ΔH in kcal/mole	Literature
$[AgCl_1]^0$	1	$1{\cdot}9 \times 10^3$	$\log K_1 = \frac{575}{T} + 1{\cdot}36$	2·65	E. Klein, *Ergeb. der intern. Konf. für wiss. Phot.* Köln (1956). O. Helwich, *Verl. Darmstadt* (1958), 225.
$[AgCl_2]^{-1}$	2	$1{\cdot}7 \times 10^5$	$\log K_2 = \frac{795}{T} + 2{\cdot}57$	3·66	E. Klein, *Ergeb. der intern. Konf. für wiss. Phot.* Köln (1956). O. Helwich, *Verl. Darmstadt* (1958), 225.
$[AgCl_3]^{-2}$	3	$5{\cdot}9 \times 10^5$	$\log K_3 = \frac{1280}{T} + 1{\cdot}48$	5·84	E. Klein, *Ergeb. der intern. Konf. für wiss. Phot.* Köln (1956). O. Helwich, *Verl. Darmstadt* (1958), 225.
$[AgCl_4]^{-3}$	4	$1{\cdot}8 \times 10^5$	$\log K_4 = \frac{3036}{T} - 4{\cdot}89$	13·75	E. Klein, *Ergeb. der intern. Konf. für wiss. Phot.* Koln (1956). O. Helwich, *Verl. Darmstadt* (1958), 225.
$[AgBr_1]^0$	1	$2{\cdot}4 \times 10^4$	$\log K_1 = \frac{620}{T} + 2{\cdot}29$	2·83	E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgBr_2]^{-1}$	2	$1{\cdot}3 \times 10^7$			E Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgBr_3]^{-2}$	3	$7{\cdot}4 \times 10^8$	$\log K_3 = \frac{2767}{T} - 0{\cdot}42$	12·62	E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgBr_4]^{-3}$	4	$7{\cdot}7 \times 10^8$			E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgBr_5]^{-4}$		$1{\cdot}1 \times 10^{11}$	$\log K_5 = \frac{4450}{T} - 5{\cdot}83$	20·3	E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgI_1]^0$	1	$3{\cdot}6 \times 10^5$			E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgI_2]^{-1}$	2	$3{\cdot}6 \times 10^{10}$			E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgI_3]^{-2}$	3	4×10^{13}			E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgI_4]^{-3}$	4	$1{\cdot}1 \times 10^{14}$			E. Klein, *Photogr. Korr.*, 92 (1956), 139.
$[AgI_5]^{-4}$		$1{\cdot}4 \times 10^{14}$			E. Klein, *Photogr. Korr.*, 92 (1956), 139.

The regions in which the different $[Ag(SCN)_n]^{1-x}$ complexes exist are shown in Figure 6.8, whereas the stability constants are listed in Table 6.2.

TABLE 6.2

STABILITY CONSTANTS OF SILVER COMPLEXES WITH THIOCYANATE IONS

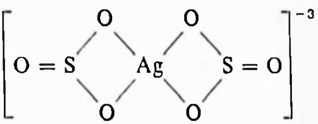
Complex	*Coordination number*	*Complex stability constants K_n at 25°C*	*Literature*
$[Ag(SCN)]$	1	$5{\cdot}5 \times 10^4$	E. Klein, *Photogr. Korr.*, **92** (1956), 139
$[Ag(SCN)_2]^{-1}$	2	$1{\cdot}67 \times 10^8$	E. Klein, *Photogr. Korr.*, **92** (1956), 139
$[Ag(SCN)_3]^{-2}$	3	$5{\cdot}6 \times 10^9$	E. Klein, *Photogr. Korr.*, **92** (1956), 139
$[Ag(SCN)_4]^{-3}$	4	$3{\cdot}7 \times 10^{10}$	E. Klein, *Photogr. Korr.*, **92** (1956), 139

6.3.3.3 *Silver complexes with sulphite ions.* The following complexes are known to be formed between silver ions and sulphite ions:

$$[Ag(SO_3)]^{-1}, \qquad [Ag(SO_3)_2]^{-3} \text{ and } [Ag(SO_3)_3]^{-5}$$

The stability constants of these complexes are listed in Table 6.3.

Of these silver complexes, $Ag(SO_3)_2^{-3}$ is the most stable. In this complex each sulphite ion is linked in the form of a chelate group to the silver ion by two oxygen atoms, and therefore the silver ion appears to have 4 coordination bonds thus forming a tetrahedral configuration in accordance with the structural formula:



In practice, this complex preponderates to such an extent that in most cases both the other complexes may be neglected.

The solubility of silver halides in sulphite solutions can be described with sufficient accuracy, e.g. by the equation (7), which was derived in paragraph 6.3.1, if only the complex $[Ag(SO_3)_2]^{-3}$ is taken into account. As an example, the solubility of silver bromide in sulphite solutions of varying concentrations at different temperatures is shown in Figure 6.9.

In the combination of sulphite and silver ions to form complexes it must be taken into account that only at high pH values the concentration of

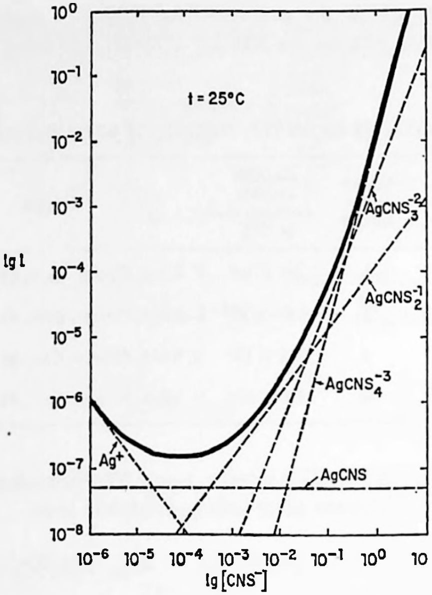


Fig. 6.7. Total solubility of silver thiocyanate complexes in the region of thiocyanate excess as a function of the concentration of free thiocyanate in the solution. Taken from E. Klein, *Photogr. Korr.*, **92** (1956), 139.

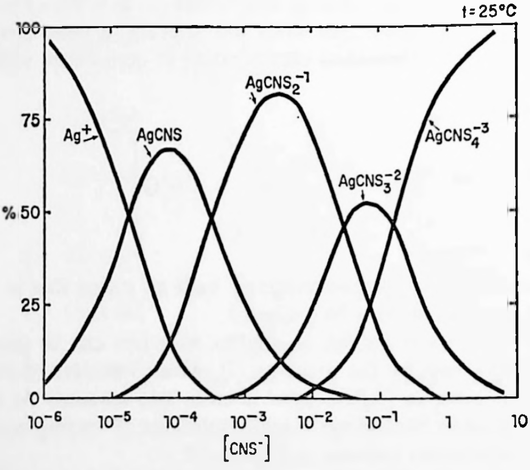


Fig. 6.8 Percentage participation of the various $(Ag(SCN)_n)^{1-n}$ complexes in the total solubility of silver thiocyanate, as a function of the free thiocyanate concentration of the solution. Taken from E. Klein, *Photogr. Korr.*, **92** (1956), 139.

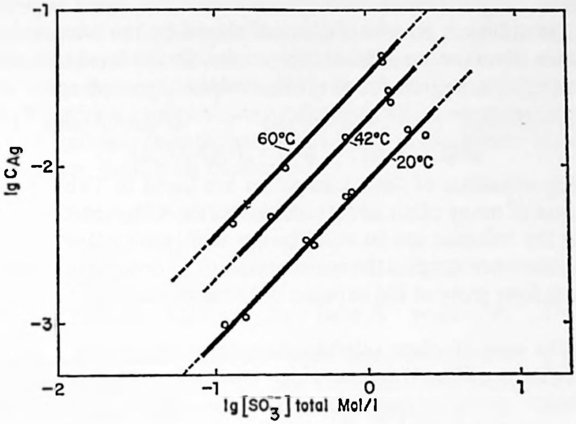


Fig. 6.9. Solubility of AgBr in sulphite solutions with the formation of complexes at 20°C, 42°C and 60°C respectively. Taken from E. Klein, *Z. Elektrochem.*, **60** (1956), 1003.

sulphite ions equals that of the sulphite ions originally present; at lower pH values (pH < 8) part of the dissolved sulphite is withdrawn from the reaction due to the protonization equilibria which exist between SO_3^{--}, HSO_3^- and H_2SO_3.

TABLE 6.3

STABILITY CONSTANTS OF SILVER COMPLEXES WITH SULPHITE IONS

Complex	*Coordination number*	*Complex stability constant K_n at 25°C*	*Dependence of the complex stability constants on temperature*	*Enthalpy of complex formation ΔH in kcal/mole*	*Literature*
$[Ag(SO_3)]^{-1}$	2	2×10^5			K. B. Yatsimirskii and V. B. Vasilev, *Instability constants of Complex Compounds*, Pergamon Press (1960), Oxford
$[Ag(SO_3)_2]^{-3}$	4	$1{\cdot}9 \times 10^8$	$\log K_2 = \frac{1185}{T} + 4{\cdot}3$	5·41	E. Klein, *Z. Elektrochem.*, 60 (1956). *1003.*
		$4{\cdot}8 \times 10^8$ (25°C)			H. Chateau, M. Duranté, B. Hervier, *Sciences Ind. Photogr.*, 3 (1956), 81
$[Ag(SO_3)_3]^{-7}$		10^9			H. Chateau, M. Duranté, B. Hervier, *Sciences Ind. Photogr.*, 3 (1956), 81

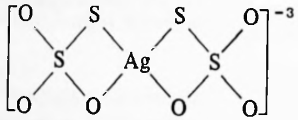
6.3.3.4 *Silver complexes with thiosulphate ions.* The most important factor, however, in the diffusion process is the part played by the complexes which are formed between silver ions and thiosulphate ions. In the literature, the following structural formulae are given for silver thiosulphate complexes:

$$[Ag(S_2O_3)]^-; \quad [Ag_3(S_2O_3)_4]^{-5}; \quad [Ag_2(S_2O_3)_3]^{-4};$$
$$[Ag(S_2O_3)_2]^{-3} \text{ and } [Ag(S_2O_3)_3]^{-5}$$

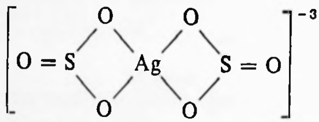
The stability constants of these complexes are listed in Table 6.4.

As in the case of many other silver complexes, the different silver thiosulphate complexes in the solution are in equilibrium with each other: with increasing thiosulphate ion concentration the concentrations of complexes which are richer in thiosulphate ions grow at the expense of those containing fewer thiosulphate ions.

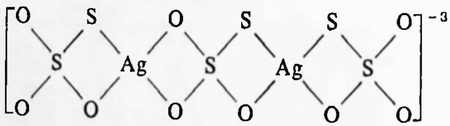
Just as in the case of silver sulphite complexes, the most stable silver thiosulphate complexes will be those in which each of two ligands is added in the form of a chelate group to the silver ion by two atoms, so that the silver ion appears to have a tetrahedral configuration.



Unlike the complex of similar composition

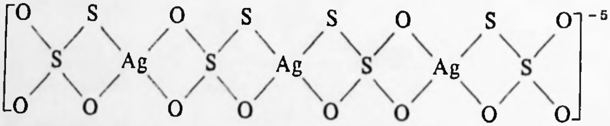


which was described in paragraph 6.3, this silver thiosulphate complex, however, is capable of adding still more silver thiosulphate groups. Thus the following polycyclic complexes are formed. These have the structural formulae:



$[Ag_2(S_2O_3)_3]^{-4}$

and



$[Ag_3(S_2O_3)_4]^{-5}$

which have already been mentioned above.

Alkali salts of silver thiosulphate complexes containing more thiosulphate ions are highly soluble in water. The alkali salts of the formula $[Ag(S_2O_3)^-$, which contain the least number thiosulphate ions, are however, except the complex lithium salt, sparingly soluble. Moreover, very many sparingly soluble compounds of intricate composition are known; these compounds probably are double salts of halides, thiosulphates and silver thiosulphate complexes. The following examples should be mentioned:

$$(NH_4)_{13} \quad Ag_5(S_2O_3)_8Cl_2$$
$$(NH_4)_4 \quad Ag_3(S_2O_3)_3Br$$
$$(NH_4)_2 \quad Ag_2(S_2O_3)\,I_2$$
$$(NH_4)_9 \quad Ag(S_2O_3)_4X_2 \text{ where } X^- = Cl^-, Br^-, I^-$$

If such sparingly soluble complex salts have precipitated, e.g. due to the exhaustion of thiosulphate ions in the solution, they redissolve in solutions containing excess thiosulphate ions only very slowly.

TABLE 6.4

STABILITY CONSTANTS OF SILVER COMPLEXES WITH THIOSULPHATE IONS

Complex	*Coordination number*	*Stability constant of complex K_n at 20°C*	*Literature*
$[Ag(S_2O_3)]^{-1}$	4	$6{\cdot}7 \times 10^8$	K. B. Yatsimirskii and V. P. Vasilev, *Instability Constants of Complex Compounds*, Pergamon Press (Oxford 1960)
$[Ag_3(S_2O_3)_4]^{-5}$	4		K. B. Yatsimirskii and V. P. Vasilev, *Instability Constants of Complex Compounds*, Pergamon Press (Oxford 1960)
$[Ag_2(S_2O_3)_3]^{-4}$	4		K. B. Yatsimirskii and V. P. Vasilev, *Instability Constants of Complex Compounds*, Pergamon Press (Oxford 1960) H. Chateau and J. Pouradier, *Sciences Inds. Photogr.* 24 (1953), 129
$[Ag(S_2O_3)_2]^{-3}$	4	$2{\cdot}85 \times 10^{13}$	H. Chateau and J. Pouradier, *Sciences Inds. Photogr.* 24 (1953), 129
		$2{\cdot}9 \times 10^{13}$	H. Chateau and J. Pouradier
$[Ag(S_2O_3)_3]^{-5}$	4	$3{\cdot}5 \times 10^{13}$	H. Staude, *Physikal. Chem. Taxchenbuch.* Vol. 2, 622 Akad. Ver. Ges. H. Chateau and J. Pouradier, *Sciences Inds. Photogr.* 24 (1953), 129

6.3.3.5 *Silver complexes with ammonia.* Just as with organic nitrogen compounds, the silver ion also forms quite stable complex bonds with ammonia.

Addition of silver ions to the free electron pair of the nitrogen atom according to the reaction:

$$Ag^+ + \begin{array}{c} R \\ | \\ |N - R \\ | \\ R \end{array} \rightleftharpoons \left[\begin{array}{c} R \\ | \\ Ag—N—R \\ | \\ R \end{array} \right]^+$$

is closely related to the addition of a proton:

$$H^+ + \begin{array}{c} R \\ | \\ |N - R \\ | \\ R \end{array} \rightleftharpoons \left[\begin{array}{c} R \\ | \\ H—N—R \\ | \\ R \end{array} \right]^+$$

As a result, the stability constants of silver complexes of the various nitrogen compounds increase with increasing pH values of the equilibrium between amine and ammonium. On the other hand, at low pH values the protons start to compete with the silver ions for the free, electron pairs of the nitrogen atoms, so that at low pH values the formation of silver complex ions diminishes.

In aqueous ammonia solutions the complex $[Ag(NH_3)_2]^+$ preponderates. The complex $[Ag(NH_3)_1]^+$ exists only in a minor concentration. Moreover, at high ammonia pressure as well as in liquid ammonia the complex $[Ag(NH_3)_3]^+$ can also be detected.

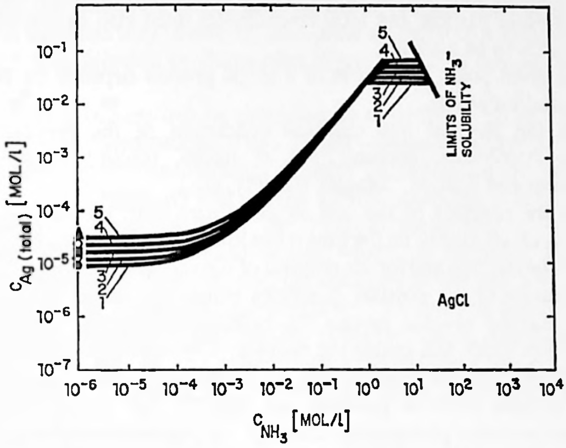
According to recent investigations the complex $[Ag_2(NH_3)_3]^{+2}$ described in the earlier literature appears to be non-existent: if hydration was involved in the older analytical results, then the older crystalline preparations to which the formula $[Ag_2(NH_3)_3]^{+2}$ had been assigned, would also have the composition $[Ag(NH_3)_2]^+$.

The solubility of silver chloride and silver bromide in aqueous ammonia solutions of varying concentrations can be obtained from Figure 6.10, whereas the complex constants are listed in Table 6.5.

TABLE 6.5

STABILITY CONSTANTS OF SILVER COMPLEXES WITH AMMONIA

Complex	*Coordination number*	*Stability constant of complex at 20°C*	*Enthalpy of formation ΔH in kcal/mole*	*Literature*
$[Ag(NH_3)]^+$	1	$1{\cdot}6 \times 10^3$		K. B. Yatsimirskii and V. P. Vasilev, *Instability Constants of Complex Compounds*, Pergamon Press (Oxford 1960)
$[Ag(NH_3)_2]^+$	2	$1{\cdot}65 \times 10^7$	12·4	R. Matejec, *Ber. d. Bunsenges. f. physik. Chem.*, 70 (1966), 703
$[Ag(NH_3)_3]^+$	3			Gmelin-Kraut-Friedheim-Peters, *Handb. d. anorg. Chem.*. 7th edition Vol. V/II, Carl Winter, Heidelberg (1914)



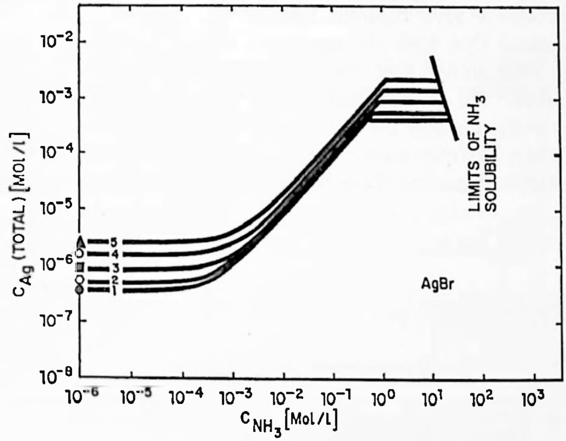


Fig. 6.10. Solubility of AgCl and AgBr in aqueous NH_3 solutions as a function of the free NH_3 concentration with variation in temperature. Taken from R. Matejec, *Ber, d. Bunsenges. phys. Chem.*, **70**, 703 (1966).

6.4 *Kinetics of the process*

It follows from the qualitative description of the processes given in the foregoing chapters (6.1 to 6.3) that the entire process is made up of a series of chemical processes (solution, development) and physical processes (diffusion).

Since these two types of process are connected with each other, any discussion of their kinetics must not only include data of the concentration and time for a definite kind of particle, but local co-ordinates must also be introduced if the description is to be accurate.

At any given point, the course of a single process depends on two possible fundamental influences.

(*a*) On the physical and chemical conditions of the process concerned (diffusion coefficients, concentration of nuclei, reaction constants during development and fixation, complex stability, etc.).

(*b*) On the coupling of the said single process with the previous and subsequent processes, that is, on the time taken for the requisite components to reach the site of the reaction and for the removal of the substances formed, respectively.

Enumeration of the possible quantities which can influence the process of diffusion transfer reversal reveals the necessity of seeking some method of simplification which will enable the problem to be dealt with conveniently.

Since, in practice, the tendency is to use increasingly shorter times of processing and because diffusion processes are likely to become of ever-increasing importance in colour processes for instance, it is of interest to consider in more detail the only article which, up to the present, is known to deal quantitatively with the process of silver complex diffusion transfer reversal.[14]

It is assumed that both the negative and the positive are saturated with developing solution and that the whole of the silver halide solvent is present in the positive. The process under discussion actually commences from the moment ($t = 0$) at which the positive and negative are brought into contact with each other. There are mainly 4 processes which have to be taken into account in a quantitative discussion of the process (see scheme of the order of reaction).

6.5 *Scheme of the order of reaction*

Process	*Negative*	*Positive*
A. Diffusion of fixing agent FA	FA_n ⟵	FA_p
B. Solution of silver halide AgHal and formation of a silver complex AgCx	+ AgHal ↓	
C. Diffusion of the silver complex AgCx		
D. Physical development on catalytically active nuclei	$AgCx_n$ ⟶	$AgCx_p$ + developer + nuclei ↓ Ag

6.5.1. DIFFUSION PROCESSES. The partial processes A and C are diffusion processes. Diffusion mainly occurs perpendicularly to the interface positive/negative. In the transition zones between the developed and non-developed areas lateral diffusion may, however, take place as observed experimentally by E. Weyde;[15] this diffusion produces edge effects similar to those described by W. Falta.[16]

The diffusion processes can be simplified by regarding them as a means of compensating the concentrations in two limited volumes (positive and negative). The rate of change in concentration depends on the difference between the concentrations of the negative and positive and on a constant D of the material. This constant comprises implicitly the diffusion coefficients of the salts in question in the respective binding agents, which are saturated with liquid, and an average distance between, and the thickness of the two layers, both of which quantities temporarily remain constant. This distance is determined by the position of the average concentrations in the two layers. On these assumptions, all the concentrations by volume may approximately be replaced by the area concentrations. The following statements apply to the temporary changes:

$$A = D_A([\mathrm{FA}_p] - [\mathrm{FA}_N]) \tag{1}$$

$$C = D_C([\mathrm{AgCx}_N] - [\mathrm{AgCx}_p]) \tag{2}$$

6.5.2 PROCESS OF SOLUTION. The process of solution B depends on the concentration of the fixing agent FA_N and on the magnitude of the area under attack. Thus in the area occupied by the silver halide grains:

$$B = K_B[\mathrm{FA}_N].\mathrm{A}_{\mathrm{AgHal}} \tag{3}$$

The area A_{AgHal} can be adequately replaced by the number of grains n_{AgHal} and the silver halide concentration [AgHal]. (All the quantities are based on unit area).

The total area A_{AgHal} is made up of the sum of the individual areas of n grains of silver halide.

$$A_{\mathrm{AgHal}} = A_{\mathrm{grain}}.n_{\mathrm{AgHal}}$$

For spherical grains:

$$A_{\mathrm{grain}} = 4\pi r^2$$

and

$$V_{\mathrm{grain}} = 4/3\pi r^3 = \frac{[\mathrm{AgHal}].V_{\mathrm{AgHal}}}{n_{\mathrm{AgHal}}}$$

When this relation has been solved for r^2 and the value obtained is introduced into the foregoing relations, the total area is given by:

$$A_{\mathrm{AgHal}} = \sqrt[3]{n_{\mathrm{AgHal}}36\pi V^2_{\mathrm{AgHal}}}\cdot[\mathrm{AgHal}]^{2/3} \tag{4}$$

In this relation V_{AgHal} signifies the volume occupied by a silver halide if the calculation is done with an absolute number of particles, or it represents the molar volume if this calculation is carried out with moles. E.g. $V_{AgCl} = 4{\cdot}28 \times 10^{-23}\,cm^3$ if the absolute number of particles is introduced into the calculation. As experiments show, the number of grains n_{AgCl} is of the order of magnitude of 10^8–10^9 per sq cm.

6.5.3 PHYSICAL DEVELOPMENT. Physical development D is conceived as a bimolecular reaction which takes place between the silver complex $AgCx_p$ and the developer E, on the surface A_{Ag} of the silver particles which have formed and consequently also depends on the magnitude of the latter

$$D = K_D . [AgCx_p] . [E] . A_{Ag} \qquad (5)$$

Thus the reaction will only proceed if, at the beginning, a certain minimum amount of nuclear silver or silver sulphide is already present. The total area again comprises:

$$A_{Ag} = A_{nucleus} . n_{Ag_2S}$$

where $A_{nucleus} = 4\pi r^2$

$$V_{nucleus} = 4/3\pi r^3 = \frac{[Ag_2S] . V_{Ag_2S} + [Ag] V_{Ag}}{n_{Ag_2S}}$$

For A_{Ag} a relation which is similar to equation (4) is obtained:

$$A_{Ag} = \sqrt[3]{n_{Ag_2S} 36\pi V^2_{Ag}} ([Ag_2S] \frac{V_{Ag_2S}}{V_{Ag}} + [Ag])^{2/3} \qquad (6)$$

where V_{Ag} and V_{Ag_2S} again represent the volumes of the particles or mole volumes of the substances in question.

For the above-mentioned substances, the following values have been obtained:

$$V_{Ag} = 1{\cdot}7 . 10^{-23}\,cm^3$$
$$V_{Ag_2S} = 5{\cdot}62 . 10^{-23}\,cm^3$$

Experiments show that the concentration of nuclei in the positive material amounts to about 10^{11}/sq cm.

6.5.4 COUPLED SYSTEM OF EQUATIONS. Of the combinations of the foregoing single processes *A–D*, there are in theory two different sequences of process:

6.5.4.1 *Cyclic sequence of processes.* The process of silver complex diffusion transfer reversal passes through the single stages *A–D*, which up to now have been considered separately.

During the physical development, D, the silver complex decomposes, thus releasing the fixing agent in its original state and making it available as a transporting agent in the positive material.

This proves to be correct to a close approximation for the cases in which thiosulphate is used as solvent for the silver halide and as a complexing agent. In this case it would be expected that, with a relatively small concentration of fixing agent, the entire quantity of silver present in the negative would also be deposited in the positive material. In fact, however, a maximum transfer of only about 60% of the silver present in the negative material could be observed (see Chapter 3).

By combining the different reaction equations A–D, the following coupled system of linear differential equations is obtained:

1. $d[FA_p]/dt = -A + (x)D$
2. $d[FA_N]/dt = +A - (x)B$
3. $d[AgHal]/dt = -B$
4. $d[AgCx_N]/dt = + B - C$
5. $d[AgCx_p]/dt = + C - D$
6. $d[Ag]/dt = +D$
7. $d[E]/dt = -\left(\frac{1}{y}\right)D$

In these equations x represents the coordination number of the complex. The silver thiosulphate complex which occurs most frequently in the conditions encountered in practice has the formula $Ag(S_2O_3)_2$, thus $x = 2$, where y represents the valency of the developer.

6.5.4.2 *Sequence of the processes which take place once.* A single cycle of fixing agent and silver complexing agent takes place when the complex decomposes at the site of development in the positive material and when the complex ligands react with the oxidation products of the developing agents which have been formed there. This is the case when sulphite is used both as a fixing agent and as a complexing agent, e.g. when various copies are produced from one and the same negative. Sulphonates which delay or prevent the further oxidation of the developer are formed. Consequently the complex ligands no longer take part in the further process of diffusion of the silver complex.

In this case the above-mentioned linear coupled system of differential equations (1–7) becomes less complicated. In the first equation in the system (1–7), the fixing agent FA in the positive material receives no supply of substance from the decomposing silver complexes. The term $(x)D$ characterizing this process cancels out.

The following system of equations is then obtained for a sequence of processes which take place once:

1. $d[FA_p]/dt = -A$
2. $d[FA_N]/dt = +A - (x)B$
3. $d[AgHal]/dt = -B$
4. $d[AgCx_N]/dt = +B - C$
5. $d[AgCx_p]/dt = +C - D$
6. $d[Ag]/dt = +D$
7. $d[E]/dt = -\left(\frac{1}{y}\right)D$

where, as before, x and y represent the co-ordination number of the complexes and the valency of the developer, respectively. The complexing agent used is sulphite: here again the complex molecule containing two sulphite ions is the form which occurs most frequently in practice.

The foregoing coupled systems of non-linear differential equations cannot be solved en bloc. The calculations for the coupled form have to be done with electronic computers.

6.6 *Single reactions*

The following is a survey of the course of reactions and of the possible effects of changing the constants.

6.6.1 DIFFUSION PROCESSES. The general equation for the diffusion processes A and C is (see equations 1 and 2):

$$\frac{dx_{1,2}}{dt} = D(x_1 - x_2) \tag{9}$$

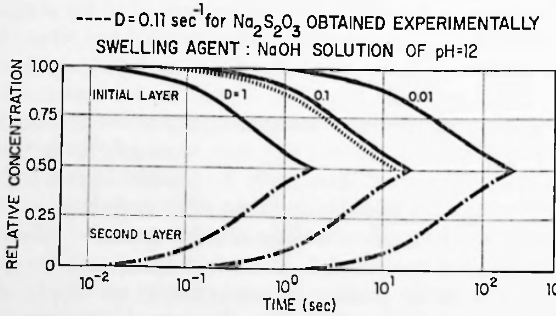


Fig. 6.11. Time function of the diffusion process for different coefficients D according to equation (10) (logarithmic time scale).

with the general conditions, $x_0 = x_1 + x_2$. After integration, the following general time function is obtained:

$$x_{1,2t} = \frac{x_0}{2}(1 \pm e^{-2Dt}) \tag{10}$$

The dependence of the process on time for different diffusion coefficients can be obtained from Figure 6.11.

Experimental investigations[17] of the kinetics of diffusion of sodium thiosulphate have shown that the diffusion coefficient depends in the first instance on the degree of swelling of the layers. On the other hand, the taking up of liquid by the layer depends not only on the type of binding agent and its degree of hardening but also on the concentration of the salt and the pH of the swelling solution. The average concentration of thiosulphate ions (FA_0) in the layers of commercial materials is $7{\cdot}5 \times 10^{17}$ per sq cm.

6.6.2 REACTION OF SOLUTION. As has already been mentioned, the solution of silver halide is an interfacial reaction, which depends not only on the concentration of the fixing agent but also and primarily on the magnitude of the available reaction area. The time function of the amount of silver halide per unit area is found by integrating the differential equation which can be obtained from equations (3), (4) and (7) as well as by determining the quantities of the substances formed. In principle, the solution of silver halide decreases hypercolically and a corresponding quantity of silver complexes is formed, i.e. the decrease in silver halide is greatest at the beginning of the reaction due to the high concentration of fixing agent and the large area.

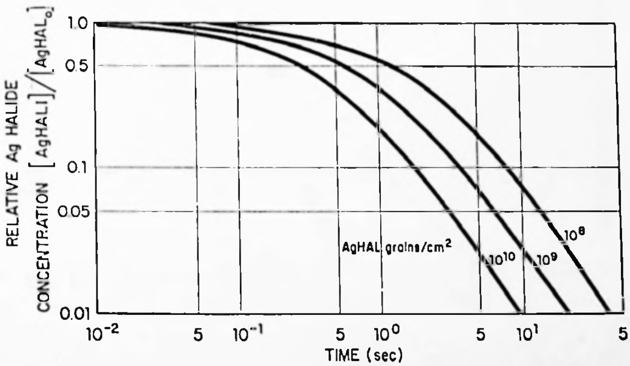


Fig. 6.12. Time function of the reaction of the solution reaction B for different grain numbers of grains n_{AgHal}. Amount of silver halide applied per unit area $[AgHal_0] = 4{\cdot}0 \times 10^{17}$/sq cm. Number of grains $n_{AgHal} = 10^8, 10^9, 10^{10}$ sq cm. Grain diameter (sphere) d = $0{\cdot}7\mu$, $0{\cdot}3\mu$, $0{\cdot}15\mu$. Concentration of fixing-agent $[FA_0] = 2[AgHal_0] = 8{\cdot}0 \times 10^{17}$/sq cm. Reaction constant $K_B = 0{\cdot}235$/sec.

Figure 6.12 shows the relative concentrations of silver halide in relation to time, the quantity of silver halide per unit area remaining constant, but in each case with the number of grains changed by a factor of 10.

Since the number of grains enters into the function in the form of its cube root, the curves of the reaction on a logarithmic time scale are shifted in a parallel direction through a distance which is equal to one third of a logarithmic time unit.

6.6.3 PHYSICAL DEVELOPMENT According to equations (5) and (6) the following differential equation applies to physical development:

$$\frac{d[Ag]}{dt} = K_D . [AgCx] . [E] \sqrt[3]{n_{Ag_2S} 36 \pi V^2 Ag([Ag_2S] \frac{V_{Ag_2S}}{V_{Ag}} + [Ag])^{2/3}} \quad (11)$$

If a developer is concerned with a one-electron transition, then:

$$[E_0] - [E] = [Ag]$$

The differential equation can only be solved en bloc if the initial concentrations of the developer and silver complex are equal to each other. This, however, does not detract from any comments which may be made.

The results of the calculation are represented graphically in Figures 6.13 and 6.14.

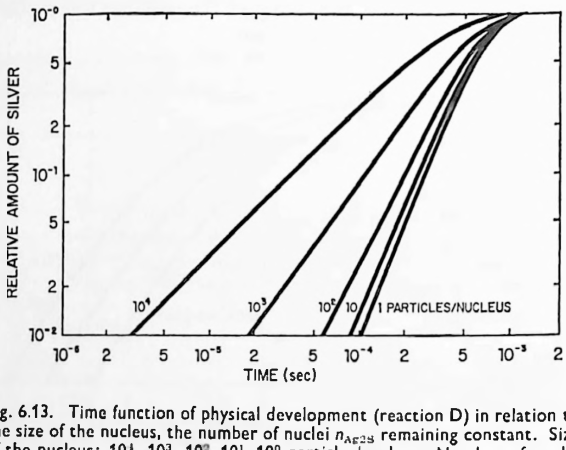


Fig. 6.13. Time function of physical development (reaction D) in relation to the size of the nucleus, the number of nuclei n_{Ag_2S} remaining constant. Size of the nucleus: 10^4, 10^3, 10^2, 10^1, 10^0 particles/nucleus. Number of nuclei $n_{Ag_2S} = 10^{11}$/sq cm. Quantity of nuclei $[Ag_2S] = n_{Ag_2S}$. nucleus size $= 10^{15}$, 10^{14}, 10^{13}, 10^{12}, 10^{11}/sq cm. Developer concentration $[E_0] = 10^{16}$/sq cm. Silver complex concentration $[AgCx_0] = 10^{16}$ sq cm. Reaction constant $K_D = 1{\cdot}125 . 10^{-12}$ cm²/sec. Molecular volume $V_{Ag_2S} = 5{\cdot}62 . 10^{-23}$ cm³, $V_{Ag} = 1{\cdot}7 . 10^{-23}$ cm³.

In the calculations the following quantities have been varied:

1. the size of the nucleus, the number of nuclei n_{Ag_2S} remaining constant and equal to 10^{11}/sq cm (Figure 6.13),
2. the size of the nucleus remaining constant and equal to 10^3 molecules (Figure 6.14).

The only effect of increasing the size of the nucleus at the same time keeping the number of nuclei constant (Figure 6.13) is to hasten the onset of development. At the end of development the size of the nucleus exerts hardly any influence. This can also be gathered from equation (11). In this equation [AG_2S] is a perturbation factor which only exerts its influence on the course of the reaction when the silver sulphide concentration is of the same order of magnitude as the silver concentration. This applies, however, only to the initial phase of development. In the final phase the silver concentration is several orders of magnitude higher than the silver sulphide concentration and only then does it determine the course of the reaction.

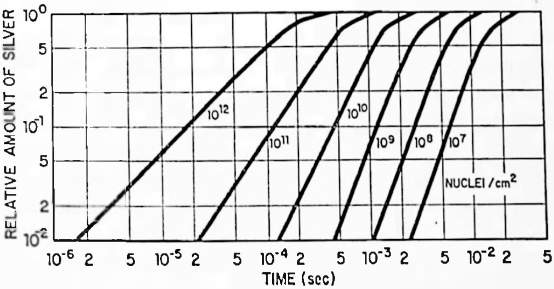


Fig. 6.14. Time function of physical development (reaction D) in relation to the number of nuclei n_{Ag_2S} with the size of the nucleus maintained constant. Size of the nucleus = 10^3 particles/nucleus. Number of nuclei $n_{Ag_2S} = 10^{12}$, 10^{11}, 10^{10}, 10^9, 10^8, 10^7/sq cm. Quantity of nuclei [Ag_2S] = 10^{15}, 10^{14}, 10^{13}, 10^{12}, 10^{11}, 10^{10}/sq cm. Developer concentration [E_0] = 10^{16}/sq cm. Silver complex concentration [$AgCx_0$] = 10^{10}/sq cm. Reaction constant $K_D = 1{\cdot}125 \,.\, 10^{-16}$ cm^2/sec. Molecular volume $V_{Ag_2S} = 5{\cdot}62 \,.\, 10^{-23}$ cm^3, $V_{Ag} = 1{\cdot}7 \,.\, 10^{-23}$ cm^3.

Things are quite different if the number of nuclei n_{Ag_2S} is varied (Figure 6.14). In this case the relation between the number of nuclei and time is similar to that which obtains in the solution reaction B. As a result of the dependence of the rate of reaction on the cube root of the number of nuclei as shown in equation (11), the course of the reaction when, in a series of tests, the number of nuclei is increased or diminished by ten, will each time be shifted on the logarithmic time scale to the left or the right by approximately one third of a logarithmic time unit. This result applies only approximately because, as has already been

mentioned, silver sulphide acts as a perturbation factor and because it implicitly contains the number of nuclei n_{Ag_2S}.

The slope of the linear region in the time curves of physical development in Figures 6.13 and 6.14 lies between the values tan $\alpha = 0{\cdot}95$ and tan $\alpha = 2{\cdot}45$. Within this range, the physical development can be replaced by the approximation function:

$$[Ag]_{rel} = At^{\tan \alpha} \tag{12}$$

In this connection it must be mentioned that the time function of the physical development which was derived under completely different conditions possesses a similar formula, in which tan $\alpha = 1{\cdot}5$.[18]

The experimental results, which have been found for the kinetics of physical development, are partly contradictory. Eggert and Arens[19] have found that the amount of reduced silver is directly proportional to the number of nuclei, but is in fact independent of the size of the nucleus. This corresponds in essence to the results of the calculation made by R. Meyer[14] for complete development. On the other hand, Rott[20] and Eggert report that a proportionality exists between the area of the nucleus and the amount of silver deposited. Calculations show that this is correct for the initial phase of development. In this connection Eggenschwiller and Jaenicke[21] point out that these differences can possibly be explained by a partial blocking of the surfaces of the inhibitors of nuclear growth (toning agents). Articles in which the density of the silver formed has been adopted as a quantity of measurement in order to examine the kinetics of development are hardly worthy of consideration, because it is precisely the case of physical development that in general no proportionality exists between the density and the amount of silver (see chapter on covering power).

However, these discrepancies in the experimental results can be explained—at least partly—by the given equation (11).

It follows from equation (11) that not only is the rate of development influenced by the number and the size of the nuclei but it is also influenced by the respective concentrations of the developer and the silver complex at the time t. When, at time t, the existing concentrations are replaced by the initial concentrations and by the amount of silver developed up to the moment, t, then we have

$$\begin{aligned}[AgK] &= ([AgK]_0 - (x)[Ag]) \qquad (12)\\ [E] &= ([E_0] - (y)[Ag])\end{aligned}$$

and when these relations are introduced into equation (11), in principle, it follows therefore that:

$$\frac{dAg}{dt} \simeq ([AgK]_0 - (x)[Ag])([E]_0 - (y)[Ag])([Ag_2S]\,\frac{Ag_2S}{Ag} + [Ag])^{2/3} \tag{13}$$

This is a polynomial containing different powers of [Ag], the highest being 8/3.

The first terms or the initial conditions [AgK_0], [E_0], x and y in the mixed terms largely determine by which exponential law the development will proceed.

6.7 *Three-stage process*

The principal rules which govern a coupled series of diffusion processes and chemical reactions can be followed more conveniently in a three-stage process. The results of the findings will now be explained by giving some examples. In these examples the sequence of the reaction is limited to the first three coupled stages:

A. Diffusion of FA from positive to negative.

B. Reaction of solution.

C. Transport of the silver complex AgCx from the negative to the positive.

Figure 6.15 shows the course of the reaction in the three-stage system with different diffusion coefficients. Case 2 is the normal one in which the diffusion processes and the process of solution take place at approximately the same speed; this is revealed by the fact that no effects of accumulation or strong suction occur with the reacting substances.

In case 1 both diffusion processes are slowed down considerably. Therefore a strong suction effect is set up during the process of solution. The concentration of fixing agent in the negative FA_N remains extremely low because the diffused fixing agent reacts immediately with the silver halide and is transformed into a silver complex. On the other hand, the silver complex formed accumulates in the negative. Because of diffusion the duration of the entire process is substantially determined by the slowest process.

The process which is determined by the reactions is shown in case 3. The diffusion coefficients have been chosen in such a way as to represent the reaction of solution as a bottleneck for the outcome of the entire process. In this case there is an accumulation of fixing agent in the negative as well as a suction action during the transport of the silver complex from the negative to the positive, and this can be recognized from the small difference in concentration between the negative and the positive.

In principle, the following can be said about badly coupled systems which are actuated by the reaction procedures described, and for which the equations hold, and in which again the entire process is determined by the result of a reaction (cases 1 and 3):

(*a*) Accumulation of the reacting substances accelerates the subsequent reaction in the diffusion processes as well as in the chemical reactions;

(*b*) Accumulation of the reacting substances retards a previous diffusion process but it does not exert any influence on the results of a previous chemical reaction;

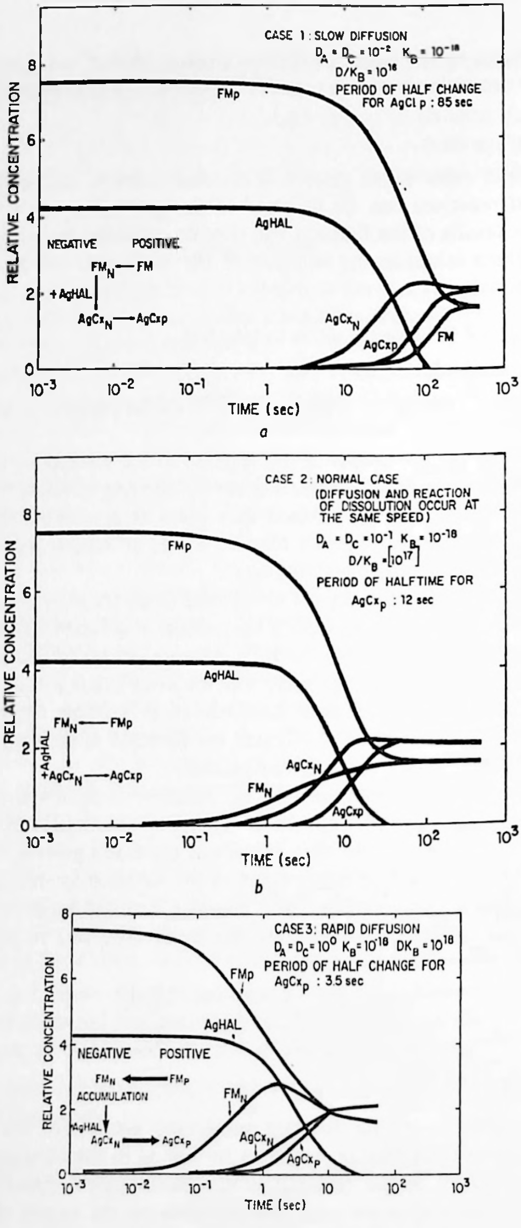


Fig. 6.15. Time function of three-stage processes consisting of:

a. Diffusion of the fixing agent FA from the positive to the negative.
b. Solution of the silver halide AgHal.
c. Transport of the silver complex AgCx from the negative to the positive (x =1).

(*c*) If, at a stage in the reaction, the concentration of a reacting substance is maintained low (suction), it accelerates a previous diffusion process.

A further statement is made on investigations of coupled three-stage processes, in which the ratio of diffusion coefficients to reaction constants is maintained constant, that is to say cases in which these quantities are changed in the same ratio. When plotted on a logarithmic time scale the outcome of the reaction is similar, except that the reaction with the larger diffusion coefficients and reaction constants is shifted by one logarithmic time unit towards shorter times.

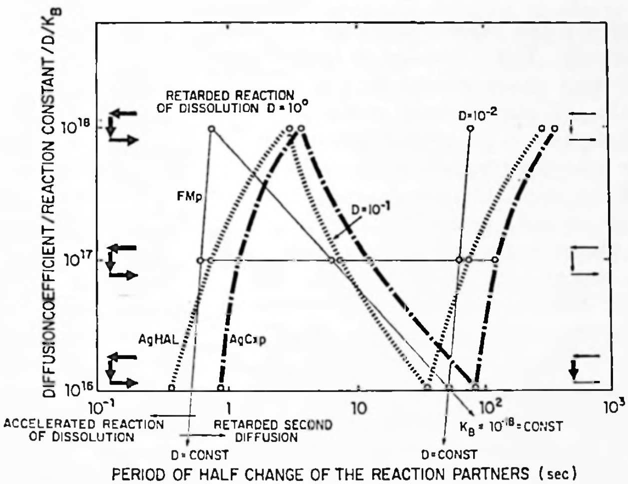


Fig. 6.16. Half-change period of the courses of reaction of FA (first stage), AgHal (2nd stage), and $AgCx_p$ (3rd stage) in the three-stage process as a function of the ratio of constants $D_{A,C}/K_B$.

This finding is of general importance because it increases our knowledge of coupled reactions.

(*d*) If the result of a reaction in a system with arbitrary diffusion coefficients and reaction constants is known, the course of any possible reaction in which the ratio of the diffusion coefficient to the reaction constant remains the same, can be predicted. The result of a coupled reaction is retarded or accelerated just as often as the constants of the original reaction are changed.

In Figure 6.16 the aforementioned experiments are summarized graphically. The quantity which was chosen temporarily to characterize the results obtained in the various stages in the reaction was the times at which the reacting substances which could not possibly give rise to accumulation phenomena

(first stage: FA_p, second stage: AgHal, third stage: $AgCx_p$) had either increased to half the final value or had fallen to half their initial value. This characteristic time is named the period of half-change.

In the diagram in Figure 6.16 the period of half change is plotted on a logarithmic scale against the ratio D/K. The curves (first stage: FA_p, continuous curve, second stage: AgHal, dashed curve, third stage: $AgCx_p$, dotted and dashed curve) illustrated the relationship between the period of half change and the ratio D/K.

From the figure the following can be concluded:

(*a*) There is a D/K value at which the three stages in the reaction are coupled optimally. This is revealed by the fact that the smallest logarithmic time difference occurs between the first and the last stages.

(*b*) In the D/K interval under consideration the result of the reaction in the first stage exerts the greatest influence on the outcome of the total reaction. The following reactions influence the result of the entire process each in a different way. This can be seen from the slopes of the various curves in the present diagram, if D or K is kept constant. If K is kept constant, the change in the diffusion coefficient is fully active in the first stage, as can be seen from the continuous straight line with the inclination of 135°, which indicates the period of half change in the first stage in the reaction. If, on the contrary, the diffusion coefficients are kept constant (practically vertical lines), it can be seen from the dashed curves which give the period of half change in the second stage that on changing the reaction constants, the influence is substantially less than was to be expected from the separate reactions. Only with a relatively large D/K ratio, when the diffusion in relation to the reaction of solution occurs practically immediately, does the dependency of the reaction constants attain the value which was to be expected from the separate reactions.

(*c*) Re-coupling of the second reaction stage to the first reaction of diffusion is relatively small. This can be seen from the slight deviation of the FA_p-straight lines from the vertical position when the diffusion coefficients are constant.

The diffusion coefficients of the first and third stages have been equated to each other in all cases. This is justified as much as it is known from literature that molecules of approximately the same size differ very little in regard to their diffusion properties. This also applies to the process in question.

6.8 *The entire process of silver complex DTR (four-stage reaction)*

The courses of the reaction in the complete four-stage processes in given circumstances can be seen from Figure 6.17. In the upper partial image the process has been calculated assuming that the negative layer contains 10^8 silver halide

grains per sq cm, whereas the lowest partial image represents the course of the reaction assuming that the negative layer contains 10^{10} silver halide grains per sq cm. The silver halide present per unit area is the same in both cases. Owing to the small silver halide surface in the upper partial image, the fixing agent accumulates in the negative. The reaction of solution begins relatively late (about one logarithmic time unit after the beginning of the first diffusion process).

In the lowest partial image, because of the much larger area, the silver halide dissolves so rapidly that no accumulation of fixing agent takes place in the negative. Unlike the three-stage process, the second diffusion process is of a completely different character in the four-stage process. The second diffusion process represents only a temporary intermediate stage. The concentration of the silver complex starts from the value 0, passes through a maximum value and returns to 0, in the negative as well as in the positive. In contradistinction to the first diffusion process, the difference in concentration in the latter case between negative and positive, a difference which exerts a decisive influence on the rate both at the beginning and the end of the process, is extremely small. As a matter of fact this difference constitutes a critical stage in the process as a whole. This process can be influenced less by a change in the diffusion coefficients than by the effect of the foregoing solution process and the subsequent developing process.

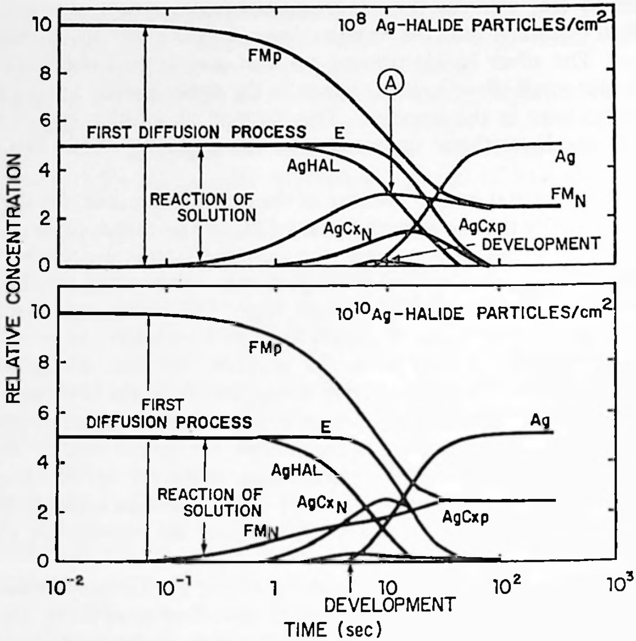
In order to obtain a large concentration gradient, the process of solution must proceed very rapidly; the concentration of the silver complex in the negative then becomes high. On the other hand, the physical development must also proceed very rapidly thereby maintaining a low concentration of silver complex in the positive. The influence of such manipulations on the whole process can be seen from Figure 6.17.

Just as in the three stage process, the experimental results can all be presented in one diagram, in which the period of half change in the separate reaction stages are plotted as a function of the ratio of the diffusion coefficients to the reaction constants. Since, in the present case, still one other reaction constant is involved, for the sake of accuracy, the diagram should be extended into the three-dimensional one.

Here again the general rule holds, that when all the diffusion and reaction constants involved are changed by the same factor (derivation of the D/K-ratio) the course of the reaction, if it is represented on a logarithmic time scale, will remain the same, and will be shifted only by the logarithmic value of the factor towards shorter or longer times on the time axis.

Figure 6.18 is a graphical representation of the relation between the half change period in the different stages in the reaction and the D/K ratios of the examples calculated. In Figures 6.18 and 6.19, K represents the combination:

$$K = K_{B,D}\sqrt[3]{n_{\mathrm{AgHal,Ag_2S}} \cdot 36\pi \,.\, V^2_{\mathrm{AgHal,Ag}}}$$



(A) ACCUMULATION OF FIXING AGENT IN THE NEGATIVE AS A CONSEQUENCE OF SLOW REACTION OF SOLUTION

Fig. 6 17. Time function of the entire DTR process. $[FA_{p0}] = 10^{18}/cm^2$. $[AgHal_0] = 5 . 10^{17}/cm^2$. $[E_0 = 5 . 10^{17}/cm^2$. $[Ag_2S] = 10^{11} cm^2$. Number of nuclei $nAg_2S = 10^{11}/cm^2$. $D_{A,C} = 10^{-1} sec^{-1}$. $K_D = 10^{-1} sec^{-1}$. $K_D = 1{\cdot}5 . 10^{-4} sec^{-1} . cm^2$. Upper partial image: slow reaction of solution —10^{8} silver halide grains/sq cm; lowest partial image: rapid reaction of solution —10^{10} silver halide grains/sq. cm.

In both of the first stages in the reaction (first diffusion process and solution process) there is no change as regards the three-stage process. The re-coupling of the subsequent stages is so weak, that in the cases examined no changes could be established. For the third reaction stage, viz. the diffusion of the silver complex, no period of half change can be given as a characteristic reaction time, because, as has already been mentioned, the concentration, after having passed through a maximum, decreases again to 0. In this case the time which it takes to reach maximum concentration, is regarded as the characteristic time. It has been plotted in the diagram in Figures 6.18 and 6.19.

In principles it can be seen in Figures 6.18 and 6.19 that the third reaction stage, viz. the diffusion of the silver complex from the negative into the positive

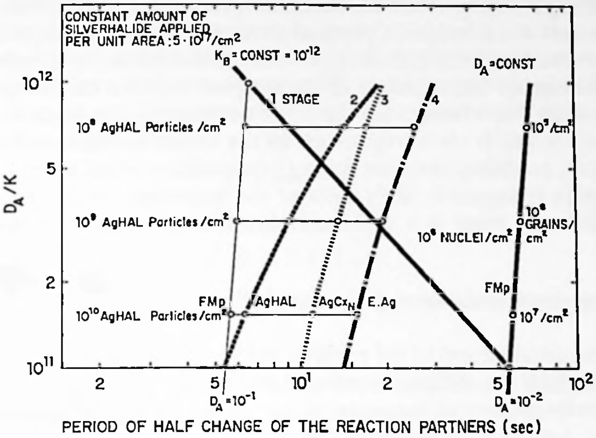


Fig. 6.18. Periods of half change of the courses of the reaction of the entire DTR process as a function of the ratio of the diffusion constant D_A to the constant of the solution reaction

$$K = K_B \sqrt[3]{n_{\mathrm{AgHal}} \cdot 36\pi V^2{}_{\mathrm{AgHal}}}$$

The number of nuclei n_{AgHal} has been varied. The remaining values correspond to the numerical data in Figure 6.19.

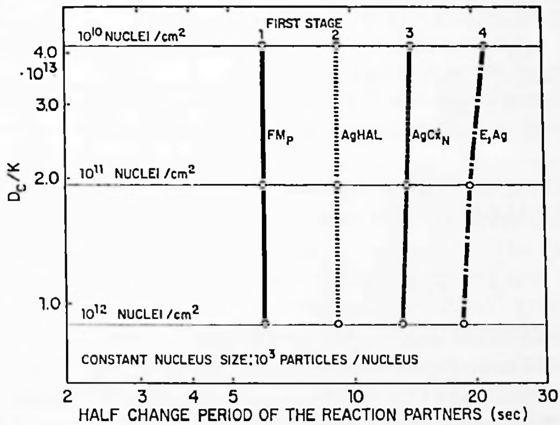


Fig. 6.19. Half change period of courses of the reaction of the entire DTR process as a function of the ratio of the diffusion constant D_C to the constant of physical development

$$K = K_D \sqrt[3]{n_{\mathrm{Ag_2S}}\, 36\, \pi V^2{}_{\mathrm{Ag}}}$$

The number of nuclei $n_{\mathrm{Ag_2S}}$ and the amount of Ag_2S nuclei but with the size of the nuclei remaining constant have been varied. The number of silver halide grains $n_{\mathrm{AgHal}} \times 10^9$/sq cm. The remaining values correspond with the numerical data in Figure 6.19.

exerts a strong levelling action on the entire process for the reasons mentioned above, whereas the subsequent physical development in the range examined is largely connected with the diffusion process. A change in the number of nuclei has no influence on the sequence of the coupled reaction in the range investigated, the main cause being that the silver complex in the positive constitutes that quantity which is obviously always in the lowest concentration.

As a result, no difficulties arise during precipitation when a small amount of silver complex is supplied. Only right at the beginning, when the area of the nuclei is still very small is a slight accumulation of silver complex observed.

6.9 *Covering power and colour of developed silver*

During the development of the positive, the silver complex, in accordance with the amount which has diffused is reduced to silver on the nuclei of the positive.

The quantity of interest, however, is not the amount of silver produced per unit of area, but the corresponding density.

As it is known from numerous investigations during physical development with previously incorporated nuclei, silver is deposited in the form of microscopically small, but compact grains, most of which are practically spherical in shape. Since these silver particles hinder the passage of light by absorption and dispersion, the density of the image is decided by the sectional area of the silver grains and not by their volume or mass.

Thus a greater density can be achieved with a large number of small grains then with an equal quantity of silver which is made up of relatively few, large silver particles of the same shape.

(The photometric constant P or its reciprocal, the covering power $1/P$, has been introduced as a measure of the density yielded by a given amount of silver.)

The covering power is given by the ratio of the density D produced and the weight of silver (g Ag) per unit area:

$$\frac{1}{P} = \frac{D}{\mathrm{Ae}}\left[\frac{\mathrm{m}^2}{g}\,;\frac{\mathrm{cm}^2}{g}\right];\, P = \frac{\mathrm{Ae}}{D}\left[\frac{g}{\mathrm{m}^2}\,;\frac{g}{\mathrm{cm}^2}\right] \tag{1}$$

In principle when the size, shape, concentration and optical behaviour of the silver grains are known the covering power can be deduced from these quantities. The first investigations in this direction were carried out by Nutting.[22]

If say a particle is struck by a beam of parallel light rays of sufficiently large sectional area F, the relative diminution in light τ caused by the particle is given by the formula:

$$\tau = 1 - \frac{\sigma}{F} \tag{2}$$

where σ is the effective sectional area of the particle, which, in general, is not identical with the geometrical projection area f.

In a layer of thickness t with a number of silver particles per unit of volume (n), the incident light weakens exponentially with increase in the thickness of the layer and in the concentration of the particles in accordance with the average effective sectional area $\bar{\sigma}$ of the particles.

$$\tau = e^{-n\bar{\sigma}t} \tag{3}$$

Hence, the density is defined by the equation:

$$D = 0{\cdot}434\, n\bar{\sigma}t \tag{4}$$

For the amount of silver per unit area Ac, the equation

$$\mathrm{Ac} = \rho_{\mathrm{Ag}} \, . \, n \, . \, \bar{v} \, . \, t \tag{5}$$

for a silver density of ρ_{Ag} and an average grain volume of $\bar{v}$ is obtained.

In general, the covering power $1/P$ is obtained from equations (4) and (5):

$$1/P = \frac{D}{\mathrm{Ac}} = \frac{0{\cdot}434\bar{\sigma}}{\rho_{\mathrm{Ag}}\bar{v}} \tag{6}$$

Thus the covering power is determined by the ratio of the average optical effective sectional area to the mean volume of the absorbing and dispersing particles in the layer.

The optical effective sectional area σ of an absorbing and dispersing particle is not independent of the method of making the measurement. When the radiation receiver is placed directly behind the layer to be measured and its dimensions are adjusted accordingly, the light which is dispersed in the forward direction will also be received. The resulting diffuse density is indicated by the symbol D_{II}. If the materials are placed in such a way that only the emerging light is received, or—what comes to the same thing—if in the most simple case the receiver is placed at a very large distance from the layer to be measured, the so-called parallel density is measured. This value is larger than the density which is obtained in dispersed light, and is indicated by the symbol $D_{\|}$. It cannot therefore be expected that the effective sectional area $\bar{\sigma}$ defined by equations (3) and (4) will be identical with the geometrical projection area f_e of the grains. The theoretical considerations of Metz[23] reveal, that when the diffuse density D_{II} is measured the effective sectional area σ_a (absorption section) coincides very approximately with the projection area f_e of the grains. Romer and Morawski[24] as well as van Veelen[25] were able to demonstrate that the absorption sectional area σ_a was always greater than the projection area f_e of the grain. For this reason the authors introduced a proportionality factor K, which gives the relation between the absorption section and projection area:

$$\sigma_a = K \, . \, f_e \tag{7}$$

The proportionality factor K itself is dependent on other factors, the most important ones being: packing density, addition of a blue-toner and grain size. If it be assumed that the diffuse density is measured, then σ in equation (6) may be replaced by equation (7). In this way the covering power is obtained as a function of the geometrical dimensions of the grain.

For the bullet-shaped silver particles, which are generally obtained in the case of the DTR-process, the following value may be derived from equation (6) and (7):

$$1/P = \frac{0{,}434}{\rho_{Ag}} \cdot \frac{3K}{2d} = \frac{0{,}65K}{\rho_{Ag}d} \tag{8}$$

in which d is the grain diameter of the silver particles. Equation (8) has been dealt with in an analogous way by Nutting.[22] It follows from this equation that the covering power is inversely proportional to the grain diameter d. Equation (8) has been checked by Ahrens, Eggert and Heisenberg as well as by Eggert and Küster[2] in the case of developed silver grains and the relation ($1/P \sim 1/d$) substantially confirmed.

Taking into account the grain size distribution for spherical particles in physical development, Klein[5] arrived at the formula:

$$1/P = \frac{0{\cdot}65}{\rho_{Ag}d} \cdot e^{-10.6\sigma^2} \tag{9}$$

where σ^2 is the square of the half-value width of a normal logarithmic distribution.

For silver grains of the order of magnitude of those which are developed in the silver complex diffusion transfer reversal process, the simple relation (8) of Nutting and the relation (9) derived by Klein is only applicable under certain conditions. Unless special measures are taken (see Chapter 3.2.2.), such metal colloids are strongly coloured. Density and covering power are no longer independent of the wavelength. The spectral absorption depends on the size of the colloidal particles on the binding agent. Figure 6.20 shows the spectral absorption of silver sols containing gelatin as the binding agent as measured by E. Klein and H. J. Metz.[28] With the increase in the grain size the colour of the light transmitted by the sols gradually changes from yellow to orange, reddish violet, through more neutral tones, greenish and brownish tones, to grey. The colour of spherical metal colloid particles has been described theoretically as a function of size and complex refractive index in relation to their environment. According to Mie,[29] a small metallic sphere is excited by the electromagnetic waves of light to give secondary vibrations, which give rise to a finite number of electromagnetic partial vibrations (dipole quadrupole vibrations, and so on).

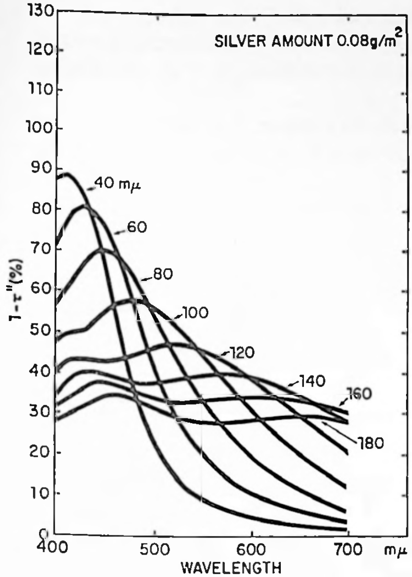


Fig. 6.20a. Absorption curves of aqueous Ag sols with different particle size $n = 1{\cdot}33$. (Silver from AgCl.)

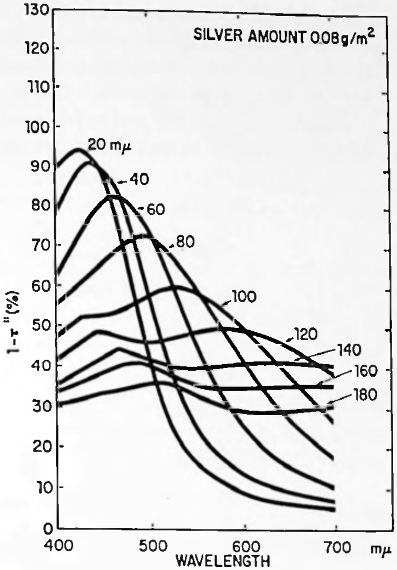


Fig. 6.20b. Absorption curves of layers, with particles of different sizes, after physical development. Diffraction index in the medium, $n = 1{\cdot}50$. (Silver from AgCl.)

The values for the absorption and dispersion coefficients for separate colloid magnitudes are obtained from the theory as a function of wavelength of the incident radiation. Absorption and dispersion are summarized in the coefficient of extinction K_λ which is related to the measurable transparency τ_λ by the following equation:

$$\tau_\lambda = e^{-K_\lambda \cdot c \cdot t} \tag{10}$$

where c (dimensionless) represents the concentration by a volume of the dispersing substance $c = n\bar{v}$. On comparing this equation with equation (3) it is seen that the extinction coefficient K_λ is the ratio $\bar{\sigma}/\bar{v}$ which H. J. Metz attempted to find.

$$K_\lambda = \frac{\bar{\sigma}_\lambda}{\bar{V}} \tag{11}$$

The extinction coefficient can be introduced directly and linearly into the formula (6) for the covering power; thus (6) can also be written as follows:

$$1/P = \frac{0{\cdot}434}{\rho_{Ag}} K_\lambda \tag{12}$$

In the above-mentioned article by Klein and Metz[28] the extinction K_λ of spherical colloidal silver particles of between 40 and 160 nm in size in a gelatin medium have been calculated as a function of the wavelength of the irradiating light in accordance with Mie's theory.

Figure 6.21 gives the extinction coefficients K_λ calculated from the article by Klein and Metz[28] as well as the covering power $1/P_\lambda$ resulting therefrom in the

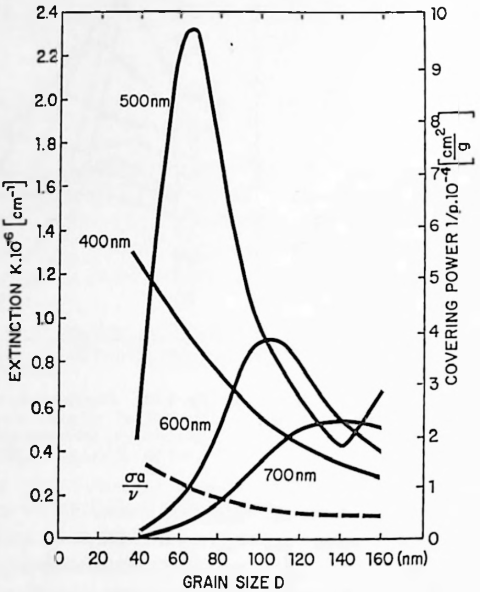


Fig. 6.21. Covering power depending on grain diameter D (compact form of the silver). Calculated from Klein and Metz.[28]

case of spherical grains as a function of the grain diameter d for different wavelengths of the measuring light. The binding agent possesses a refractive index $n = 1{\cdot}5$ (gelatin).

In the main it can therefore be concluded that with particles of less than 120 nm, in diameter, the resulting covering power will be very greatly dependent on the wavelengths of the measuring light. Only when the particles exceed the above dimensions can approximately congruent results be expected, i.e. it is only grains of this order of magnitude which yield somewhat grey or black image tones.

If the shape of the silver particles deviates from a sphere, the spectral absorption will also change. Calculations have only been made for ellipsoids.[30] In

principle, however, it appears from the differences in the spectral properties of a sphere and an ellipsoid, that the colour can be shifted towards the generally desired neutral grey image tone not only by changing the particle size and the binding agent, but also by appropriately shaping the particles during development. Obviously, the blue toning agents are covering by adsorption parts on the surface of the grains thus causing irregular growth to take place (see chapter 3.2.2). However, the tone of the image can also be changed by another method which, in certain conditions, is related to the above mentioned change in form which is brought about by the use of additives.

The calculations cited above have been carried out under the assumption that the packing density of the grains is sufficiently low to prevent the grains from exerting any mutual influence on their dispersing properties. However, this assumption does no longer hold for the conditions obtaining in silver complex diffusion transfer reversal, at least at the higher densities.

Weyde, Klein and Metz[31] have shown that when the packing densities of nuclei is sufficiently high during physical development, the growing silver grains can agglomerate to form larger aggregates as is shown diagrammatically in Figure 6.22.

The average number of particles m per aggregate is derived from statistical observations as a function of the concentration by volume c of the particles.

$$m = \frac{8\, ln \dfrac{1}{1-c}}{1-(1-c)^8} \qquad (13)$$

The function $m = f(c)$ represented in Figure 6.23 shows that the mean size of an aggregate greatly increases when the concentration by volume c exceeds 10%.

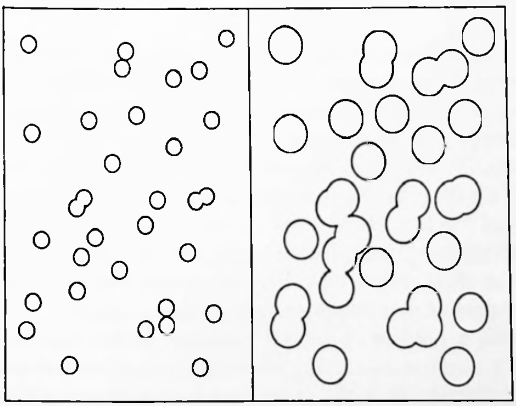


Fig. 6.22. Schematic representation of the formation of multiple aggregates.

Simultaneously with the formation of larger aggregates and with a concentration by volume of silver higher than 3%, the colour of the silver deposited changes to black almost independently of the size of the individual particles. In this case, the conditions (spherical particles, no interaction) for the absorption curves in Figure 6.20 and the values of the extinction or covering power shown in Figure 6.21 are no longer given. This effect is employed in most of the layers used in practice. The multiple dispersion which occurs at these high concentrations of silver increases the absorption of the incident light and consequently also the density and covering power.

By way of example, the covering power of a positive which has been produced by silver complex diffusion transfer reversal is presented as a function of density in Figure 6.24.

The covering power is seen to depend greatly on the density. With increase in the density, the covering power diminishes hyperbolically. If it be assumed that silver is deposited on all the nuclei present, then the size of the nuclei will change with increase in the supply of silver whereas the number of grains will remain constant. Since to the first approximation, the covering power obtained in accordance with equations (8) or (9) is indirectly proportional to the grain diameter d, the above effect of the decrease in the covering power with increase in the quantity of silver deposited can readily be understood.

If, in equation (4), the optical effective sectional area is equated to the absorption sectional area:

$$\bar{\sigma}_e = \bar{\sigma}_a = \frac{\pi}{4} \cdot d^2$$

and if relation (4) is introduced into equations (8) or (9), the hyperbolical relation which is found to exist between covering power and density will then be given by:

$$1/P \simeq D^{-1/2} \tag{14}$$

The values of covering power which can be obtained in a positive copy which has been prepared by silver complex diffusion transfer reversal are extremely high in comparison with these which can usually be obtained with silver halide emulsions. According to the aforesaid articles,[25,26] the values of the covering power $1/P$ of negative emulsions according to grain size lie between about 0·2 and 2·0 sq m/g. On the other hand, Figure 6.24 shows values of covering power of between 13 and 5 sq m/g. Even when it is taken into account that the density values have been measured using incident light and at least at low densities are twice as large as these which have been measured using transmitted light, relatively high values of covering power are always obtained.

For this reason, a positive of normal gradation in the tone values can be developed with a negative containing relatively little silver and possessing an extremely flat gradation. In addition to the covering power ordinate $1/P$, the ratio $\bar{\sigma}/\bar{v}$ has been plotted in Figure 6.24 as a further ordinate scale: this can be

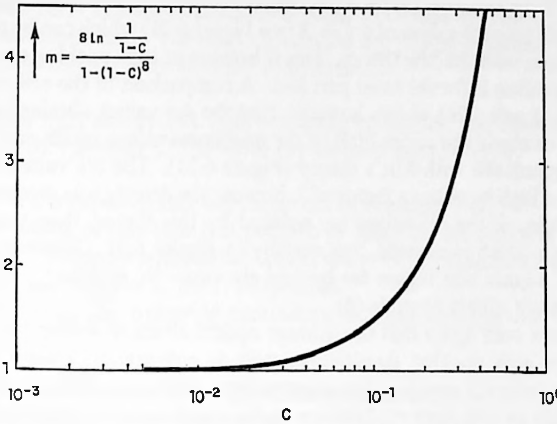


Fig. 6.23. Mean aggregate size (m) in function of the volume concentration (c).

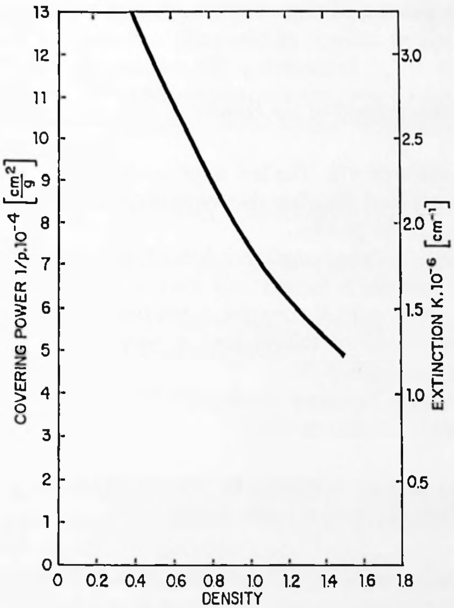


Fig. 6.24. Covering power depending on the density (calculated).

calculated from equation (6) for a physical development. No direct comparison can be made with the values of $\bar{\sigma}/\bar{v} = K$ (see Figure 6.21) which can be calculated in accordance with the Mie theory. This is because at high packing densities the strong coloration is for the most part lost. A comparison of the ordinate scales (Figures 6.21 and 6.24), shows however, that the $\bar{\sigma}/\bar{v}$ values obtained in Figure 6.24 lie at or above the upper limit of the maximum values which can be calculated in accordance with Mie's theory (Figure 6.21). The $\bar{\sigma}/\bar{v}$ values in Figure 6.24 are too high by about a factor of 2, because the density was measured using reflected light. If the $\bar{\sigma}/\bar{v}$ values are reduced by this factor, then they will lie in the range which is covered theoretically in Figure 6.21. However, they lie entirely in a grain size region far beyond the ratio $\bar{\sigma}/\bar{v} = 3/2d$ to be expected from Nutting's simple formula (8).

This shows once again that the average optical effective section of area σ_e in the case of high packing densities as well, is substantially larger than the absorption sectional area σ_a. The measurement of covering power does not in itself provide an adequate explanation of the absolute value of σ: the number of nuclei per unit area or the average grain volume v must also be known. Articles in which a method is described for determining the number of nuclei or the average grain volume as a function of the amount of silver deposited in practical conditions (high packing density, addition of blue-toning agents) are not yet available.

6.10 *The DTR Development of the Positive*

6.10.1 MODEL EXPERIMENTS. The last stage in the DTR-process is the reduction on catalytic nuclei of the silver thiosulphate complexes which have diffused from the negative to the positive.

What is the nature of these complexes? According to Chateau and Pouradier[32] the $Ag(S_2O_3)_3^{5-}$ complex is formed only when the thiosulphate concentration exceeds 1·5 *M*. In a normal negative + positive DTR-sandwich therefore, where the concentration of thiosulphate is never higher than 0·1 *M*[33], the complex can only be $Ag(S_2O_3)_2^{3-}$.

A special technique has been developed[34,35,36] to study the reduction on nuclei of complex silver salts in vitro.

6.10.2 GENERAL RUN OF EXPERIMENTS. Varying quantities of the following solutions are mixed in a beaker while stirring:

(*a*) $Na_2S_2O_3$ solution + $AgNO_3$ solution, which yield the complex salt $Na_3[Ag(S_2O_3)_2]$;

(*b*) Buffer (Na_3PO_4 + Na_2CO_3 + gelatin) + suspension of nuclei + toners (if required). Development is started by the addition of:

(*c*) Developer. The development is brought to an end by adding:
(*d*) Dilute acetic acid. The resulting samples are further examined in relation to the time of development in order to determine:

(1) their light absorption, light scattering properties, and silver content
(2) the morphology of the silver (by electron microscopy).

Details of the experimental technique can be found in 6.11.
In experiments of this type it is possible to study the reduction of the silver thiosulphate complexes without the complication of the simultaneous diffusion phenomena which occur in the DTR-process.
The influence of the following parameters has been investigated:

(1) the nature and concentration of the nuclei
(2) the concentration of the silver thiosulphate complex
(3) the ratio of silver/thiosulphate
(4) the composition of the developer
(5) toners.

Physical development was followed by means of silver analyses and density measurements, and the growth of the nuclei by electron microscopy.
The kinetics of the reduction are still controversial.
According to Meyer[37] it is a bimolecular reaction, which takes place between the silver complex and the developer on the surface of the nuclei and is therefore dependent on this area:

$$\frac{d[Ag]}{dt} = K[Ag(S_2O_3)_2^{3-}]\,[\text{developer}].n.(\text{Area})$$

where n is the number of nuclei per unit volume and (Area) the average area of a single nucleus.
We shall review the results of the model experiments in order to find out how well they agree with this kinetic formula.

6.10.3 THE NUCLEI

6.10.3.1 *The Chemical Composition of the Nuclei.* According to Eggert and Arens,[38] it is only the number of nuclei and not their dimensions or composition which is important. Rott,[39] on the other hand, finds that silver sulphide nuclei are more active than silver nuclei. In practice, it is generally accepted that the DTR-process is influenced both by the number of nuclei and by their chemical composition. This is clearly born out by the effect which their composition has on the image tone.

A distinction has however to be made between the start of the reduction, when the nuclei still retain their original character, and the further stages in which e.g. the silver sulphide nuclei are covered with reduced silver.

It is, therefore, to be expected that the effect of the chemical composition of the nuclei will primarily be felt at the start of reduction.

The method of preparation of the nuclei also exerts an influence. Silver nuclei were made by the reduction of silver nitrate with dextrin in a gelatinous medium (Carey Lea Sol). Silver sulphide nuclei were prepared by adding a solution of silver nitrate to a sodium sulphide solution with vigorous stirring. The kinetics of development are given in Figures 6.25, 6.26 and 6.27. Silver sulphide nuclei made in the presence of a large excess of sulphide are less active than those made with excess silver.

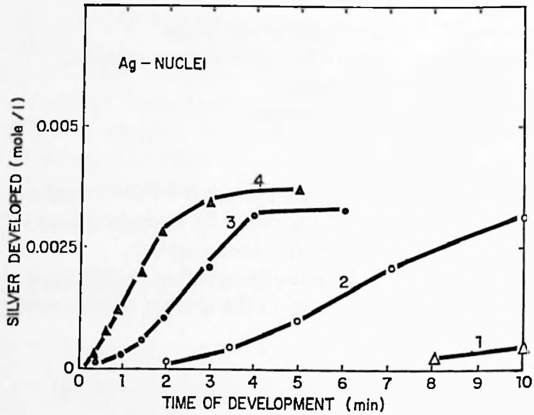


Fig. 6.25	*mole Ag/l*	*Number of Ag nuclei/ml*
1	0	0
2	$2{\cdot}8 \times 10^{-6}$	$1{\cdot}3 \times 10^{10}$
3	$7{\cdot}0 \times 10^{-5}$	$3{\cdot}3 \times 10^{11}$
4	$8{\cdot}4 \times 10^{-4}$	4×10^{12}

Fig. 6.25. Silver nuclei.

The induction period of the reduction is shorter with silver nuclei than with silver sulphide nuclei.[35] The rate of development is also higher in the ascending region in the curve when silver nuclei are used, and this, in spite of their being fewer in number. However, it is difficult to decide whether this is due to slower reduction or to the greater spread of the induction periods of individual silver sulphide nuclei.

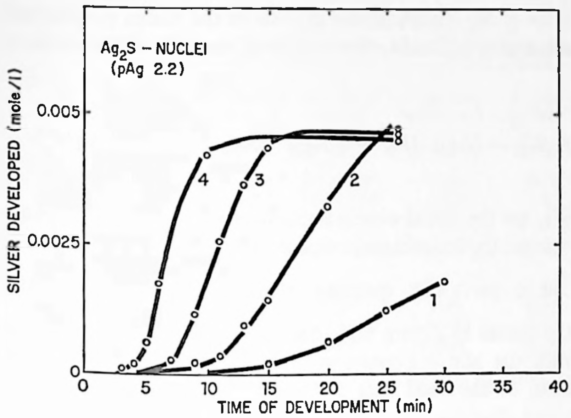


Fig. 6.26. Silver sulphide nuclei, $pAg = 2{\cdot}2$.

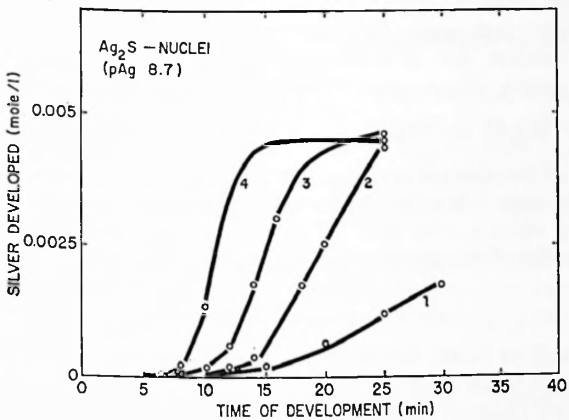


Fig. 6.27. Silver sulphide nuclei, $pAg = 8{\cdot}7$.

Figs. 6.26 and 6.27	*mole Ag_2S/l*	*Number of Ag_2S Nuclei/ml*
1	0	0
2	$1{\cdot}4 \times 10^{-6}$	$2{\cdot}5 \times 10^{11}$
3	$1{\cdot}4 \times 10^{-5}$	$2{\cdot}5 \times 10^{12}$
4	$1{\cdot}4 \times 10^{-4}$	$2{\cdot}5 \times 10^{13}$

Developer: hydroquinone + Phenidone* + Na_2SO_3 + Na_3PO_4 pH 11·7

Complex: $AgNO_3$ 0·0055 mole l
$Na_2S_2O_3$ 0·0275 mole/l

Diameter of the spherical nuclei obtained from electron-microscope observations:

silver 160 Å
silver sulphide 70 Å

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6.10.3.2 *Concentration of the Nuclei.* If the growth of the nuclei is spherical and the rate of reduction proportional to the total area, the rate of the reaction is given by:

$$\frac{d[Ag]}{dt} \sim n^{1/3} \cdot ([AgK]_0 - [Ag])\,([E]_0 - \tfrac{1}{2}[Ag])\,\left([Ag_2S]\frac{v_{Ag_2S}}{v_{Ag}} + [Ag]\right)^{2/3}$$

where $[AgK]_0$ and $[E]_0$ are the initial concentrations of the silver thiosulphate complex and the developer (hydroquinone) respectively.[37]

When $\log \frac{d[Ag]}{dt}$ at a particular quantity of developed Ag is plotted against $\log n$ from the curves in Figure 6.25, the slope of the line obtained is 0·33, as expected from the above expression. This shows that the rate of reaction is proportional to the total area of the nuclei when these are silver nuclei.

With silver sulphide nuclei the slope is smaller (0·20 to 0·25).[36] This might be due to the nuclei being more widely distributed in size or shape at the outset. It is worth noting, however, that, in addition to spherical growth, a certain amount of tabular growth always occurs. Since in the straight-line region of the curve $[Ag] \gg [Ag_2S]$, the term $[Ag_2S] \frac{v_{Ag_2S}}{v_{Ag}}$ becomes negligible and cannot be the cause of the observed deviation (Plate 6.2).

The increase in thickness is less than the increase in diameter so that here we must find a value which is lower than 1/3 for the exponent of n. This is especially noticeable with silver sulphide nuclei which are produced at a high pAg.

6.10.3.3 *Dimensions of the Nuclei.* The catalytic activity of a blue silver sol was compared with that of a yellow silver sol.[36]

The yellow silver sol consisted of spherical particles of an average area of 0·000462μm^2. During reduction, the growth of polyhedra was clearly observed. However, departures from a spherical shape were small enough to be neglected (Plate 6.3).

The blue silver sol consisted of flattened particles of an average area of 0·01554 μm^2 and an average volume of 0·00008784 μm^3. During reduction these grew into hexagonal platelets (Plate 6.4).

The reciprocal induction period (τ_{0i}^{-1}) is a measure of the rate of reaction at the start of reduction. This quantity would be expected to be proportional to the total area of the nuclei. In the later stages of development the rate of reaction $(d[Ag]/dt)_{max}$ is no longer determined by the area of the nuclei but rather by the (number of nuclei)$^{1/3}$ [37].

The data in the table show no proportionality between the total area of the

TABLE 6.6

CATALYTIC ACTIVITIES OF BLUE AND YELLOW SILVER SOLS

	Conc. nuclei mole/l	*Number of nuclei/l*	*Total area nuclei (cm^2)*	*d Ag/dt* mg. min^{-1}*	τ_0^{-1}† min^{-1}
yellow silver sols	$0{\cdot}93 \times 10^{-5}$	$2{\cdot}4 \times 10^{13}$	110	0·67	0·167
	$2{\cdot}8 \times 10^{-5}$	$7{\cdot}2 \times 10^{13}$	330	1·06	0·250
blue silver sols	$2{\cdot}8 \times 10^{-5}$	$3{\cdot}3 \times 10^{12}$	510	0·45	0·100
	$0{\cdot}93 \times 10^{-4}$	10^{13}	1530	0.77	0·156
	$2{\cdot}8 \times 10^{-4}$	$3{\cdot}3 \times 10^{13}$	5100	0·98	0·392
	$0{\cdot}93 \times 10^{-3}$	10^{14}	15300	1·15	1·000

* Maximum gradient.

† The reciprocal induction period, the induction period being taken as the point at which the extended straight-line region of the development curve intersects the time axis.

nuclei and the reciprocal induction period, when the results with the yellow and blue silver sols are compared.

In the case of the blue silver sol it is questionable whether the total area is significant since most of the silver is deposited at the edges of the nuclei. Here a distinction must probably be made between the active area and the total area. The edges make up only about 10% of the total area. If we take only this edge area into account a better correlation of area with reciprocal induction period is found.

Tabular crystal growth of gold has often been described in the literature. Yuen-sheng Chiang and Turkevich[10] have found that laminar growth results from the aggregation and reorientation of smaller gold particles at the edges of a crystal.

6.10.3.4 *Catalytic Activity of the Nuclei.* If the growth of the nuclei is spherical and the rate of reduction proportional to the total area, the same relation of 6.10.3.2 may be applied.

Past the induction period when $[Ag_2S] \ll [Ag]$ this expression reduces to:

$$\frac{d[Ag]}{dt} \sim ([AgK]_0 - [Ag])\,([E]_0 - \tfrac{1}{2}[Ag])n^{1/3}\,[Ag]^{2/3}$$

The rate of formation of silver $d[Ag]/dt$ is therefore a complex function of [Ag]. The term $[Ag]^{2/3}$ arises from the proportionality between catalytic activity and the total area. Therefore $d[Ag]/dt$ might be expected to increase with the development time. Both the concentration of the complex and of hydroquinone however decrease during development, so that $d[Ag]/dt$ actually decreases with longer development times.

The pAg also exerts an influence. The higher the pAg, the slower the development even when the concentration of the complex is kept constant. Apparently the above expression for d[Ag]/dt is too simple and should contain an additional term to take the dependence on pAg into account. Since the value of pAg increases during development, this must also contribute to the decrease in d[Ag]/dt.

In the model experiments[35] it is found that d[Ag]/dt increases greatly only at the beginning of the reaction and then levels off to a constant value (Figures 6.25, 6.26, 6.27). It would appear that any increase in the rate of reaction caused by the growth in the catalytic area is compensated by a reduction in the rate as a result of the increase in the pAg and the decreasing concentration of the reactants.

Cole and Pontius[41] have also found a very slight dependence of d[Ag]/dt on the amount of silver formed, i.e. $[Ag]^{1/5}$. They observed this effect with both of the Kodak Colour Developers 4-amino-N,N-diethyl-3-methyl-aniline monohydrochloride (CD-2) and 4-amino-3-methyl-N-ethyl-N-(β-methyl-sulfonamidoethyl) aniline sesquisulphate monohydrate (CD-3) and with a metol hydroquinone developer.

These authors worked with gelatin layers and attributed the weak dependence of d[Ag]/dt on [Ag] to the fact, that most of the nuclei are inactive because they lie deep down in the layer and are relatively inaccessible. This explanation cannot be advanced to account for our own observations since in this case all the nuclei have an equal chance of reacting.

6.10.4 THE CONCENTRATION OF THE SILVER THIOSULPHATE COMPLEX. According to Cole and Pontius[41] the rate of reduction of silver thiosulphate complexes increases with the logarithm of the silver ion concentration. They observed this with CD-2, CD-3, and MQ developers.

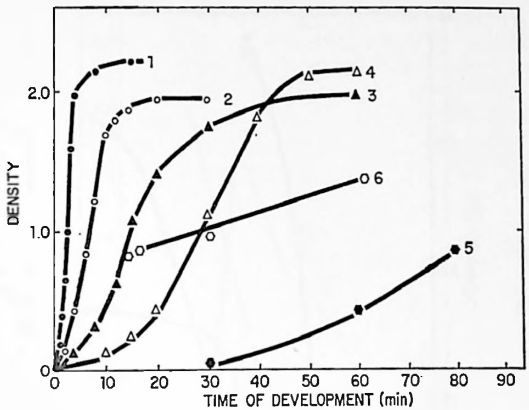
With PQ-developers a similar increase is observed.[35,36]

Figure 6.28 shows how the induction period lengthens and the reduction rate decreases with increase in the concentration of thiosulphate. A sudden addition of thiosulphate during the reduction also quickly slows down the reaction (curve 6).

The concentration of silver nitrate is kept constant and thus the concentration of the complex $[Ag(S_2O_3)_2^{3-}]$ also remains constant. This presupposes that no higher complexes are formed. Measurements of the Ag potential do in fact confirm that only 1–2 complexes can exist in these conditions.

Meyer's expression[37] d[Ag]/dt $\sim$ $[Ag(S_2O_3)_2^{3-}]$ should in fact be completed by a term which takes into account the influence of the pAg on the rate of reduction.

The influence of the pAg is also observed when the total concentration of the complex is lowered while keeping the ratio of silver to thiosulphate constant.[36] Lowering the total concentration by a factor of 2 brings about a decrease of



	Conc. (mole/l)		pAg
	$Na_2S_2O_3$	$AgNO_3$	
1	0·0110	0·0055	9·6
2	0·0165	0·0055	10·8
3	0·0275	0·0055	11·9
4	0·0550	0·0055	12·8
5	0·110	0·0055	13·5
6	0·0275 towards 0·110 after 14 min.	0·0055	

Fig. 6.28. Developer: Phenidone + hydroquinone, nuclei: Ag_2S, $2{\cdot}8 \times 10^{-6}$ mole/1.

0·3 units in the pAg which, in turn, results in a perceptible reduction in the induction period (Figure 6.29).

With Phenidone* and hydroquinone the induction period is shorter than with hydroquinone alone[43] but the dependence on the pAg is similar.

The most noticeable feature in Figure 6.29 is that the slope of the curves decreases with decrease in the concentration of the complex. In Figures 6.30a and 6.31a this slope is plotted against the concentration of the complex for silver and silver sulphide nuclei respectively. In Figures 6.30b and 6.31b the slopes and reciprocal induction times of the same curves are shown as a function of the pAg.

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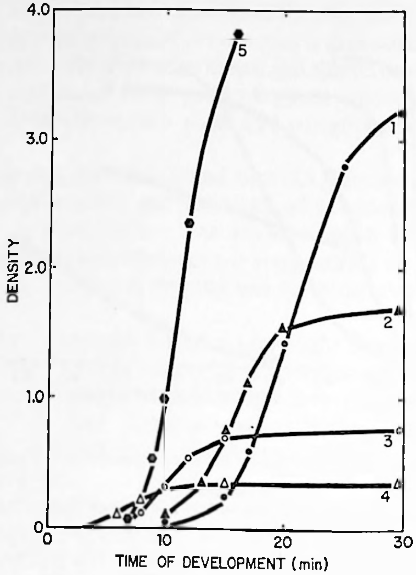


	$AgNO_3$ *(mole/l)*	*$Na_2S_2O_3$* *(mole/l)*	p*Ag*
1	0·0055	0·0275	11·58
2	0·0028	0·014	11·20
3	0·0014	0·007	10·91
4	0·0007	0·0035	10·62
5	0·0083	0·0275	10·91

Fig. 6.29. Developer: hydroquinone, nuclei: Ag_2S, $1{\cdot}4 \times 10^{-6}$ mole/1, complex conc.: see table.

In Figure 6.30a we can see how the rate of reduction, expressed as the increase in density per unit time, first increases with the concentration of the complex, passes through a maximum and finally decreases again. Such behaviour is to be expected if we make the rather plausible assumption that the silver thiosulphate complex which is adsorbed to the nuclei, reacts. According to Jaenicke and Fütterer[44] the silver thiosulphate complex is adsorbed more strongly to silver than is the thiosulphate ion which is also adsorbed.[45]

At the higher concentration the complex will partially cover the surface and prevent the developer from reaching it. This amounts to a competitive process and will therefore slow down the development.

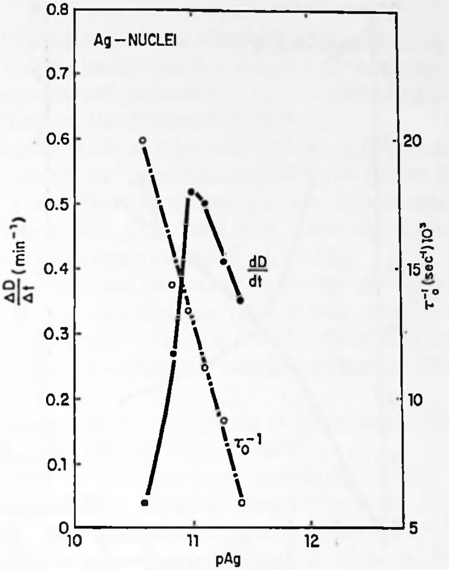


Fig. 6.30a

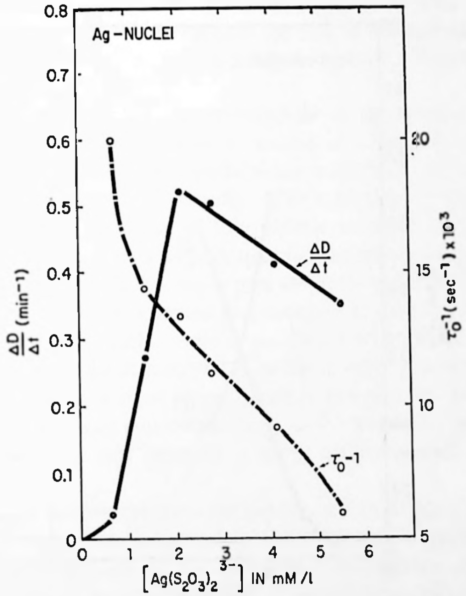


Fig. 6.30b

Nuclei: Ag 2·8 × 10^{-5} mole/1 (1·3 × 10^{14} nuclei/1)
Developer: Phenidone + hydroquinone
——— the rate of reaction as a function of the concentration of the complex (Fig. 6. 30a) and of the *p*Ag (Fig. 6.30b).
— — — reciprocal induction period.

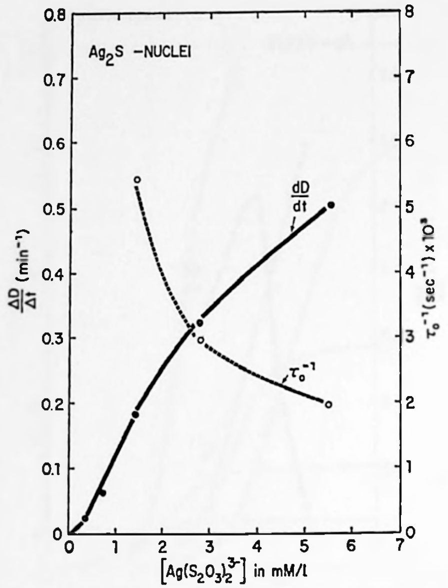


Fig. 6.31a

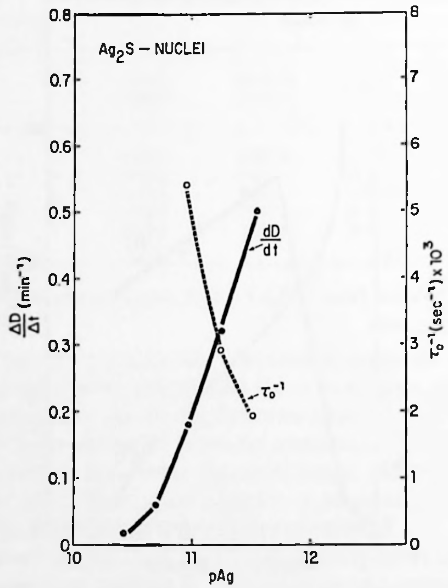


Fig. 6.31b

Nuclei: Ag_2S 1·4 × 10^{-5} mole/1 (2·5 × 10^{15} nuclei/1)

Developer: Phenidone + hydroquinone

——— the rate of reaction as a function of the concentration of the complex (Fig. 6.31a) and of the *p*Ag (Fig. 6.31b).

— — — reciprocal induction period.

The reciprocal induction period is a linear function of the pAg (Figure 6.30b). The influence of the pAg on the induction period is probably due to the increased adsorption of hydroquinone promoted by the adsorbed silver ions. This hypothesis is due to Pontius, Newmiller and Cole.[46]

With silver sulphide nuclei no maximum is observed (Figure 6.31a). Since the total area of the nuclei was approximately 3·7 times greater than that of the silver nuclei, it is possible that an eventual maximum would only occur at higher concentrations than those used here. Here too the induction period increases sharply with increase in pAg (Figure 6.31b).

A proportionality between the rate of reduction and the concentration of the complex is observed only when the ratio of silver nitrate to thiosulphate is kept constant. If more silver nitrate is added—which does not alter the concentration of the complex—the rate of reaction is increased (see curves 1 and 5 in Figure 6.29).

What are the concentration ratios in the DTR-process? Here the induction period is very short if a PQ developer is used.[47]

The induction period can be made very short in the "in vitro" experiments by keeping the concentration of the silver complex very low. A high density can, however, be obtained by adding a solution of complex during the reaction.[36]

If we may extrapolate from the model experiments to the DTR-system, this means that the concentration of the silver thiosulphate complex in the positive layer will not reach a high value because the rate of the reduction is large in comparison with the diffusion. This is in agreement with Meyer's scheme and is confirmed in practice.

The initial concentration of the thiosulphate in the positive will decrease rapidly as a result of diffusion and the formation of a complex with silver from the negative. After this, silver thiosulphate complexes will diffuse to the positive in the form of the 1–2 complex. The reduction of this complex will not actually start until the ratio of thiosulphate to silver in the positive has become sufficiently low, i.e. a certain quantity of silver complex must have diffused to the positive while the major part of the thiosulphate initially present in the positive must have been bound as a complex in the negative. It is worth noting that, on a molar scale, there is an excess of silver halide over thiosulphate[48,49,50] so that the concentration in the positive can decrease rapidly.

During the reduction of silver thiosulphate in the positive, thiosulphate ions are released and these ions can diffuse back to the negative. In this manner a single thiosulphate ion can serve as a silver carrier several times (cascade theory).[48,49,50]

The thiosulphate concentration in the positive will reach an equilibrium value when as much thiosulphate is formed by the reduction reaction as is removed by diffusion to the negative. If the reduction is accelerated by a more active developer, the equilibrium concentration of thiosulphate will, for instance, be increased. This will in turn cause more of the complex to diffuse from the

negative and raise the concentration of silver thiosulphate complex in the positive.

Analogous conditions could be obtained in our model experiments by increasing the concentration of the complex while keeping the ratio of silver to thiosulphate constant. It seems therefore that the rate reaction is proportional to the concentration of the complex[37] under practical conditions as well.

6.10.5 THE COMPOSITION OF THE DEVELOPER

6.10.5.1 *Comparison of Developers.* Fairly active PQ developers are generally used in the DTR-process.[47]

It it well-known that Phenidone and hydroquinone form a super-additive developer for silver halide emulsions. A similar superadditivity has been observed in the physical development of silver thiosulphate complexes on nuclei (Figure 6.32).[35,43,51]

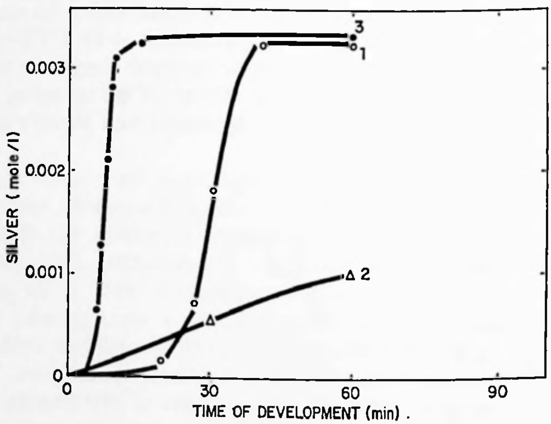


Fig. 6.32. Superadditive development Nuclei: Ag_2S 1·4 × 10^{-0} mole/1

1. hydroquinone (0·0048 mole/1)
2. Phenidone (0·0006 mole/1)
3. hydroquinone + Phenidone (0·0048 mole/l and 0·0006 mole/l).

Since the induction period is shortened and development in the straight-line region of the curve is accelerated as well, this superadditive behaviour must be attributed to the regeneration of the adsorbed Phenidone as in the case of normal silver halide emsulsions.

During the reduction, hydroquinone monosulphonate is formed. This compound also forms a very active superadditive mixture with Phenidone so that one mole of hydroquinone is able to reduce more than two moles of silver. Brinckman[49] has found that, in the DTR-sandwich, one mole of hydroquinone can yield 3·4 moles of silver, which proves that the monosulphonate also plays a role in the total reduction process.

Used alone, hydroquinone is a slow developer with a long induction period. Silver sulphide nuclei precipitated at a low *p*Ag give a shorter induction period than those precipitated at a high *p*Ag. This may be due to the silver ions assisting the adsorption of hydroquinone.[46,52]

With silver nuclei, hydroquinone sulphonate when used alone gives an even longer induction period than does hydroquinone. With silver sulphide nuclei there is practically no difference between the two developing compounds (4a).

Phenidone and *p*-phenylenediamine derivatives show a much shorter induction period than does hydroquinone.[35,41]

6.10.5.2 *The Concentration of Hydroquinone.* In Figure 6.33a the rate of the reaction, characterized either as the slope of the straight-line region in the D vs time curve or as the reciprocal induction period (τ_0^{-1}), is plotted as a function of the concentration of hydroquinone.

If the rate of reaction is defined as the reciprocal induction period: it is approximately proportional to the concentration of hydroquinone. Defining the rate of reaction $\Delta D/\Delta t$ in the straight-line region in the curve, the rate is proportional to (hydroquinone)$^{0\cdot75}$ except at the lowest concentrations where the dependence is of a still lower order.[36]

Figure 6.33b shows the rate of development as a function of pH, when the concentration of the hydroquinone is kept constant.

Between a pH value of 10 and 10·6 the rate of reaction is proportional to the concentration of the OH-ions. At higher pHs this dependence decreases. At a pH of 12, at which hydroquinone has completely dissociated into the divalent anion, it is independent of pH.

6.10.5.3 *The Salt Concentration.* Cole and Pontius[41] have found that the rate of reduction of a silver thiosulphate complex is influenced by the nature of the buffer. Sodium salts give faster development than potassium salts and phosphates are faster than carbonates. These results were obtained with coatings of colloidal silver nuclei on films.

The same phenomenon is observed in solution.[35] The acceleration of development caused by salts depends on the concentration of gelatin and is probably due to the reduction of the negative zeta-potential brought about by the high salt concentration.

Pontius, Cole and Newmiller[53] have determined the activation energy of the development of a silver thiosulphate complex in gelatin layers by a CD-3

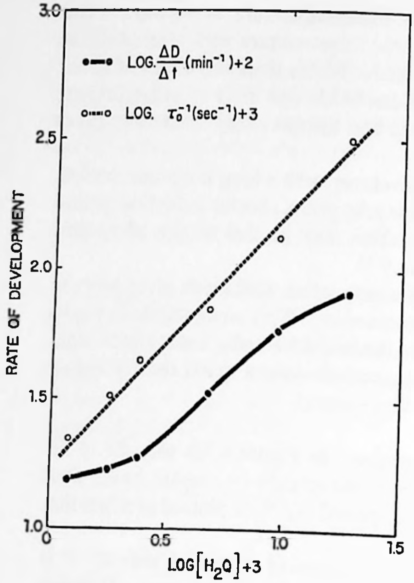


Fig. 6.33a. Dependence of the rate of reaction on the concentration of hydroquinone (in the absence of Phenidone).
Nuclei: Ag_2S 1·4 × 10^{-5} mole/l.

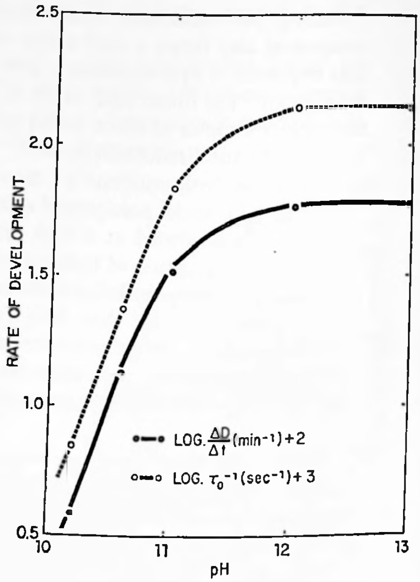


Fig. 6.33b. Dependence of the rate of reaction on pH. Conc. of hydroquinone 0·0048 mole/l (no Phenidone).
Nuclei: Ag_2S 1·4 × 10^{-5} mole/l.

developer. They found a value of 7·5 kcal/mole thus showing that diffusion is the factor which determines the rate of development.

At a high temperature the silver thiosulphate complex is more dissociated. This causes the *p*Ag to decrease. Pontius *et al.* compensated for this by adding more thiosulphate.

TABLE 6.7

INFLUENCE OF SODIUM SULPHATE ON REDUCTION OF SILVER THIOSULPHATE BY HYDROQUINONE

Gelatin content	$t_{D\,0\cdot5}$ (min)*		$t_{D\,1-2}$ (min)*	
	NaOH	*NaOH + 40 g Na_2SO_4/l*	*NaOH*	*NaOH + 40 g Na_2SO_4/l*
0·006%	18	12	11	7
0·06%	26	10	15	6
0·3%	34	9	17	6
1·2%	44	8	20	5

Hydroquinone 0·0048 mole/l, pH 11, silver nuclei 2·8 × 10^{-5} mole/l.

* $t_{D\,0\cdot5}$(min) is the time in minutes necessary to obtain a density of 0·5. $t_{D\,1-2}$(min) is the time necessary to obtain a density increase from 1 to 2.

Van Veelen, Berendsen and de Meyer[35] carried out similar experiments with hydroquinone. They found an activation energy of 22 kcal at a low salt concentration and of 15 kcal at a high salt concentration. If compensation had been made for the change in pAg in these experiments, lower values for the activation energy would probably have been found, but this effect would most likely have been roughly the same at high and at low salt concentrations. The more rapid development observed at a high salt concentration cannot therefore be due to faster diffusion since then one would find an activation energy of 5 to 7 kcal (the rate of diffusion is determining) at low salt concentration and a higher value (the rate of the chemical reaction is determining) at a high salt concentration.

In the normal DTR-process, the developer is always very concentrated and no supplementary salt effect is observed.

6.10.5.4 *Influence of Bromide and Iodide Ions.* Potassium bromide has no effect on the reduction of silver thiosulphate complexes. Thiosulphate ions and silver thiosulphate complex are both adsorbed to metallic silver.[44,45] Evidently bromide ions cannot displace these ions.

Iodide ions slow down the development considerably,[35,46] Newmiller and Pontius have shown that, in the absence of air, only about 5% of the area of a silver wire is covered but that, in the presence of air, a complete monolayer is formed. Apparently the adsorption of iodide depends on the adsorption of silver ions to the silver nuclei.

Iodide ions have little effect on the induction period of hydroquinone development but exert their primary effect after the induction period. This would point to competitive adsorption between iodide and hydroquinone ions.

6.10.6 TONERS. In order to obtain a neutral image tint toners are used in the DTR-process. Most of the compounds mentioned in the patent literature are heterocyclic mercaptans.

6.10.6.1 *Phenyl tetrazole thiol.* The best-known of these toners is 1-phenyl-1H-tetrazole-5-thiol. This compound is adsorbed strongly to silver.[54,55] In the absence of oxygen or silver ions, it forms a monolayer on a silver surface. In the presence of silver ions the adsorption is increased to several layers. These silver ions can be obtained simply by allowing the system to react with oxygen.

The rate of physical development is very much reduced by phenyl tetrazole thiol.[56] Newmiller and Pontius have studied the effect of adsorption on the activity of a developer. They found that the activity of an MQ developer was directly proportional to that fraction of the surface of the nuclei which was not covered by phenyl tetrazole thiol.[54]

Brinckman and van Veelen[47] have found that phenyl tetrazole thiol also reduces the rate of DTR-development by Phenidone and hydroquinone. The induction period is also lengthened. Figure 6.34 shows the results of a model experiment on the reduction of silver thiosulphate complex on silver sulphide nuclei in the presence of various concentrations of phenyl tetrazole thiol.

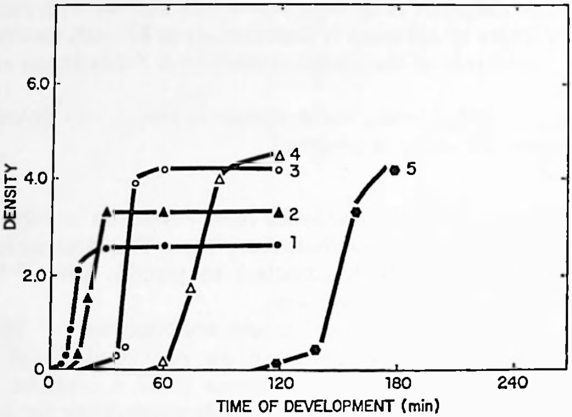


Fig. 6.34. The reduction of a silver thiosulphate complex solution as a function of the concentration of phenyl tetrazole thiol.

Nuclei Ag_2S ($1{\cdot}4 \times 10^{-6}$ mole/1)
Developer: standard PQ
Conc. Phenyl tetrazole thiol (PTT)
1. no PTT
2. $5{\cdot}6 \times 10^{-6}$ mole/l
3. 11×10^{-6} mole/l
4. 17×10^{-6} mole/l
5. 22×10^{-6} mole/l

The induction period decreases with increase in the concentration of nuclei,[36] as shown in Table 6.8.

When the surface of the nuclei is completely covered with PTT, development does not commence. This is in accordance with the results obtained by Pontius, Newmiller and Cole,[46] except for one important difference. The MQ developer used by Pontius *et al.* shows no induction period whereas the one which was used in these model experiments shows a clear induction period. This difference is due to the presence of sulphite which completely alters the shape of the development curves. It causes both the appearance of an induction period and a subsequent accelerated development.

If we assume that the induction period is caused by the adsorption of complex silver thiosulphate, which prevents the developer from being adsorbed to the nuclei, it is evident that the additional adsorption of PTT can only lengthen the induction period. During this period a slight amount of development still occurs and this brings about an increase in the amount of catalytic silver. More

TABLE 6.8

DECREASE OF INDUCTION PERIOD WITH INCREASE IN CONCENTRATION OF NUCLEI

Mole PTT/l	*Induction period (min)*				
	No nuclei	*Silver nuclei area 300 cm²*	*Silver 3000 cm²*	*Silver 3 m²*	*silver sulphide 4 m²*
0	10	3	2	0·33	
$5{\cdot}7 \times 10^{-6}$	77	14 (13%)*	3 (12%)	0·10 (7%)	
$11{\cdot}3 \times 10^{-6}$	148	52 (29%)	17 (27%)	0·25 (17%)	
$17{\cdot}0 \times 10^{-6}$	308	163 (52%)	44 (48%)	2·5 (28%)	
$22{\cdot}6 \times 10^{-6}$		404 (68%)	259 (64%)	5 (40%)	6
$34{\cdot}0 \times 10^{-6}$				15 (61%)	
$45{\cdot}2 \times 10^{-6}$				44 (79%)	
$56{\cdot}7 \times 10^{-6}$				∞(99%)	21
133×10^{-6}				∞	∞

* Percentage of the surface occupied by PTT. These values were calculated on the basis of the adsorption isotherm of Newmiller and Pontius.[54]

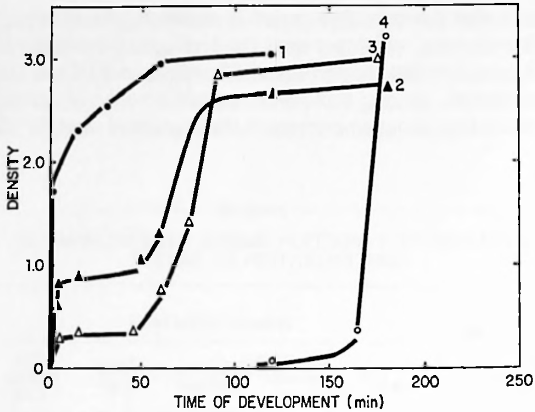
PTT is adsorbed to this newly formed silver until eventually the concentration of PTT becomes so low that it can no longer inhibit the reduction. From this time onwards development becomes very rapid.

At a pAg $< 10{\cdot}7$ peculiarities show up in the development curve (Figure 6.35).

These peculiarities are probably due to the formation of the silver salt of PTT. At a ratio of thiosulphate to silver of two (curve 3 in Figure 6.35), the solution has a pAg-value of 9·6. At this silver-ion concentration and a concentration of PTT ($56{\cdot}7 \times 10^{-6}$ mole/l) the solubility product of the silver salt of phenyl tetrazole thiol, which is of the order of 10^{-15} to 10^{-16}, is exceeded.

It seems likely that the formation of the silver salt assists development, possibly by being more readily reducible than the thiosulphate complex.

A similar effect has been observed by Klein, Münch and Treichel in the development of DTR-material.[57] They found that the reduction was not so much inhibited by the addition of the silver salt of PTT as by the PTT itself. They attribute this to the silver salt acting in the capacity of additional nuclei.



	Conc. mole/l	
	$Na_2S_2O_3$	*$AgNO_3$*
1	0·0070	0·0055
2	0·0092	0·0055
3	0·0110	0·0055
4	0·0140	0·0055

Fig. 6.35. Reduction of complex silver thiosulphate in the presence o
PTT 56·7 × 10^{-6} mole/1
Nuclei Ag_2S
Standard PQ-developer.

6.10.6.2 *Other Mercapto-derivatives.* Many other toners are described in the patent literature. Most of them are also mercapto-derivatives. The fact which is usually emphasized is that they cause little or no slowing down of the development. A reduced rate of reaction is apparently not essential for obtaining a neutral tint.

Van Veelen and Brinckman[58] have studied six mercapto-derivatives in detail:

I. 1-phenyl-2-imidazolidine-thione
II. 1-phenyl-1H-tetrazole-5-thiol (PTT)
III. 6-methyl-perhydro-1, 3-thiazine-2-thione
IV. perhydro-1, 3-thiazine-2-thione
V. N,N-bis(5-methyl-2-thioxo-oxazolidine-3-yl-methyl)-methylamine
VI. 4,5-diphenyl-4-imidazoline-2-thione.

The compounds I to V all yield a neutral tone. Their effect on the rate of reduction of the complex silver thiosulphate is however very different (Figure 6.36).

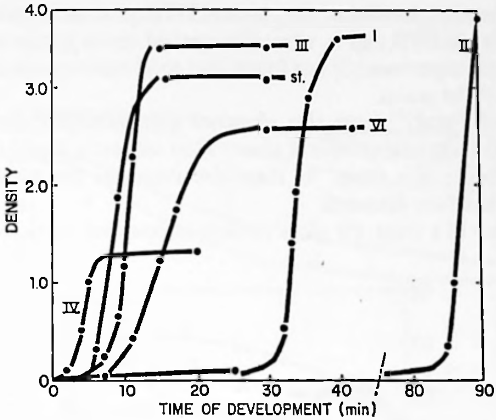


Fig. 6.36. Rate of reduction with different mercapto compounds

st.	without mercapto compound
I	2 mg/l of I
II	3 mg/l of II
III	2 mg l of III
IV	10 mg/l of IV
VI	10 mg/l of VI

6.10.6.3 *Mechanism of Toning*. This subject is treated at length in section 3.2.4. The most important factors affecting image toning are:

(1) increased average grain size as a result of the poisoning of the less active nuclei and the relatively greater growth of the most active nuclei;[59]
(2) higher concentration by volume of the nuclei, leading to the easier formation of aggregates;[59]
(3) non-spherical grains resulting from a crystal growth which is disturbed by the presence of a toner on the surface of the nuclei.[34] Spherical particles can be dealt with by the Mie scattering theory.[60] Departures from this shape cause a change in the spectrum. The Mie theory should be adapted. The image probably remains, at least qualitatively, the same since a similar relation between the absorption and grain size is found for both spherical and tabular grains.[61]
(4) changes in the optical properties of the grain surface which alter its reflectivity. If the toner makes the grain surface less smooth this might bring about such a change.

The influence of toners on the colour and morphology of the silver deposited on the nuclei in vitro has been studied by van Veelen and Brinckman.[58]

From the experimental point of view this method is much simpler than that

of studying the silver formed in the practical DTR-process. Since the effect of toners is similar in DTR and in vitro, this method seems justifiable.

In these model experiments it was found that good toners profoundly changed the structure of the grains.

Ohyama and Futaki[62] have also observed that mercapto derivatives profoundly change the crystal growth of silver. They reduced a liquid silver chloride sol in the presence of a toner. In these circumstances the grains were more compact and had finer filaments.

In the absence of a toner, the silver consists of compact particles with regular

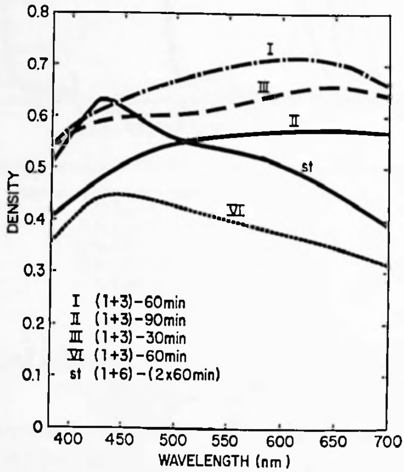


Fig. 6.37. Transmission spectra of silver developed without a toner (st.) and with the compounds I, II, III and VI.

contours (Plate 6.5). This is not true for silver formed in the presence of a toner With III the silver appears to be an aggregate of smaller particles (Plates 6.6 and 6.7). With II, at a high concentration, where strong inhibition is evident, filament formation has even been observed (Plate 6.8).

Figures 6.37 and 6.38 show the absorption and reflection spectra of the developed silver.

Wavelength shifts in the absorption maximum are caused by changes in grain diameter. In the absence of a toner, these shifts are small and the spectra are in qualitative agreement with the Mie theory of scattering. The occurrence of a second maximum for the largest grains is also predicted by theory (see Table 6.9).

The absorption spectra of grains which are grown in the presence of a toner however no longer fit in with the theory. The shift to longer wavelengths with

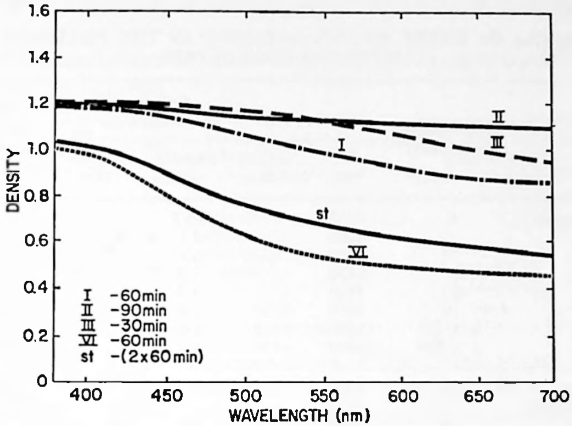


Fig. 6.38. Reflection spectra of silver developed without a toner (st.) and with the compounds I, II, III and VI.

increase in particle diameter is more pronounced and a second maximum does not occur.

The influence of toners is especially noticeable in the reflection spectra.

Similar results were obtained in experiment with DTR-material.[47] To avoid any effect of packing on the results, the positive layer was removed from

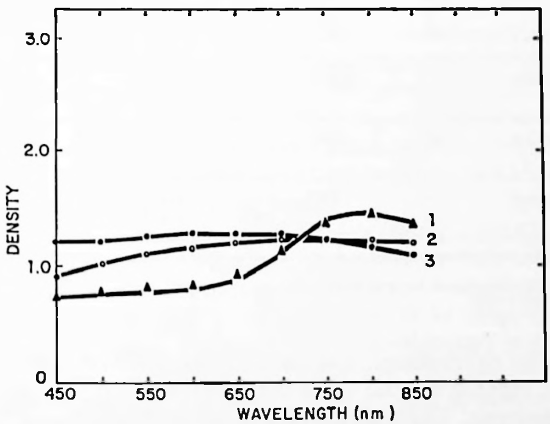


Fig. 6.39. Absorption spectra of colloidal silver.

1. no PTT added
2. 1·1 × 10^{-5} mole/l PTT
3. 2·2 × 10^{-5} mole/l PTT

Nuclei: silver (Argyrol) 2·8 × 10^{-3} mole/l.

TABLE 6.9

SPECTRA OF SILVER GRAINS OBTAINED IN THE PRESENCE OF MERCAPTO COMPOUNDS

	Development time (min)	*λ max (A)*		*Colour ratio D_{450}/D_{700}*		*Average* diameter (A)*
		1st max.	*2nd max.*	*Transmission*	*Reflection*	
Reference	6	4250		16·5		150
	7	4400		15		300
	7½	4450		15		580
	9	4550		7.5		660
	11	4800		3·7	1·2	890
	30	4960	4250	2·9	1·2	930
	2 × 60†	(5600)	4300	1·6	1·4	1210
	3 × 60†	(6800)	4450	1·4	1·6	1370
(toner) Compound I	36	4300		2·0	1·0	300
	37	4350		1·9	1·0	550
	38	5100		1·3	1·0	810
	40	6000		1·1	1·1	1080
	60	6200		1·0	1·3	1120
Compound II	85	4000		2·3	1·0	
	86	4600		1·8	1·0	
	90	6600		0·9	1·1	
Compound III	7	4200		3·2	1·0	
	8	4400		2·7	1·0	
	9	4650		1·7	1·0	680
	10	5200		1·3	1·0	890
	11½	5900		1·1	1·2	1020
	14	6300		1·0	1·2	1190
	30	6400		0·9	1·3	1200
Compound IV	15	6000		0·9	1·4	2000
Compound V	40	4900		2·1	1·0	700
Compound‡ VI	16	4700		1·5	1·7	1000
	60		4400	1·4	1·7	1100

* For toners I and III, the diameter of the aggregate is given. With toner II the grains are very irregular and no diameter is given.
† Obtained by multiple reduction on the same nuclei.
‡ Compound VI is not a toner.

the support after development, and the resulting silver sol diluted. Here too it was observed, that the dimensions of the grains were not the only factor determining the spectrum. Unfortunately the presence of gelatin made it difficult to determine the grain structure accurately. With the non-inhibiting thiazine derivative (III) the grain structure was certainly very irregular.

Toners are useful with silver nuclei as well as with silver sulphide nuclei. This is illustrated by Figure 6.39 where PTT was used.

Without PTT the silver is blue in colour, but with PTT it has a neutral tone.[43,63]

At higher concentrations of nuclei more toner is of course needed to maintain a neutral tone, as follows:

Conc. PTT (mole/l)	$[Ag_2S] = 1{\cdot}4 \times 10^{-6}$ *mole/l* *area 0·066 m²* *number of nuclei: 10^{15}*	$[Ag_2S] = 1{\cdot}4 \times 10^{-5}$ *mole/l* *area 0·66 m²* *number of nuclei: 10^{16}*
$5{\cdot}7 \times 10^{-7}$	little effect	
$17{\cdot}1 \times 10^{-7}$	grey-brown	
$28{\cdot}4 \times 10^{-7}$	grey-black	
$5{\cdot}7 \times 10^{-6}$	black	little effect
$11{\cdot}3 \times 10^{-6}$		grey-brown
$29{\cdot}6 \times 10^{-6}$		black

In order to understand the mechanism of the toner action a few more experimental data must be mentioned.[36] The toner must be present from the very beginning of development. If it is added when the reduction has been only 3% completed, a slight effect is still observed. If added when the reduction is 10% complete, there is no effect whatever. Nor is this due to a slow adsorption of the toner. If the reduction is first brought to a halt by lowering the pH and the mercapto derivative is given half an hour to be adsorbed before the reduction is started again by raising the pH to 11, the image tone is not affected.

The image tone can be changed from brown to lilac-blue by a brief etching with dilute potassium ferricyanide, and without perceptibly changing the grain size.[34] Presumably this treatment alters the surface structure and thereby causes a departure from Mie scattering.

Although it is not possible to change the image tone by adding a toner after development, it is possible to render it less neutral by the subsequent deposition of silver in the absence of a toner. This is a clear proof that it is not so much the size of the grains as their shape which determines the image tone.

The adsorption of mercapto derivatives to the nuclei strongly disturbs their growth. This growth starts at only a few places on the surface and in this manner yields a cluster of small spherical particles.

It is well known that the formation of aggregates can change the colour of gold particles from brown to blue.[64,65] It is quite possible that the effect of toners in the DTR-process is produced by the same mechanism.

The thiazine derivative (III) is adsorbed weakly to silver and is probably desorbed by the developer. Accordingly the development is not inhibited to any significant extent. It is not clear however how a compound which does not slow down development can influence crystal growth. If development starts in a few well-defined places and its rate is proportional to the catalytic area, a slowing down in the development ought to be expected.

As far as we know there is no theory of the scattering of light by aggregates of small particles in existence. The Mie theory is only strictly valid for spherical

particles. Calculations by Gans[66] for elliptical particles and experiments by Wiegel[61] with tabular silver particles have shown that the shape of the grains has an effect on the spectrum. It still remains questionable however whether the effect of toners can be explained entirely in terms of the shape of the grains.

The adsorption of mercapto derivatives is certainly not a factor since their addition after development does not alter the image tone.

The experiments of Turkevich[65] however, have shown the importance of clustering in determining the image tone and such structures have been found to occur in DTR.

In this context, the work of Stevens[67] must be mentioned. He found that the surface-to-volume ratio was very important in determining image tone. The larger this ratio, the blacker the silver appears. An irregular surface gives a more neutral tone than a regular one. A cluster necessarily has a greater surface-to-volume ratio than a sphere of the same diameter.

The details of crystal growth in the presence of toners is still not known and will require further experimental work.

During preparation of the manuscript two new papers dealing with silver-image tone have been published.

Berry and Skillman[68] calculated the absorption spectra of silver spheres with a diameter lower than 100 Å after the Mie theory. There was a large discrepancy between theory and experiment, which they ascribed to a difference between the optical properties of bulk silver and these of small particles.

They also showed that impurities can shift the absorption spectrum to shorter wavelengths or can decrease its height or both at the same time. Adsorption of 1-phenyl-1H-tetrazole-5-thiol reduces the peak height without shifting the position very much. The particles used by Berry and Skillman had a volume average diameter of 56Å. In DTR practice the silver particles have larger diameters and less influence of adsorbed 1-phenyl-1H-tetrazole-5-thiol on the absorption spectrum is to be expected. In our vitro experiments, addition of toner after completion of development had no effect.

Solman,[69] in an important paper dealing with the covering power of silver deposited by physical development, discusses the effective methods of tone modification. Of practical value are those which lead to (*a*) asymmetric or irregular-shaped particles, (*b*) clusters of particles, or (*c*) toner adsorbed on the silver particles. In our vitro experiments, examples of both (*a*) and (*b*) were shown.

6.11 *Synopsis*

In vitro, model experiments constitute a powerful tool in the study of the last stage in the DTR-process, i.e. the physical development on the nuclei. They make it possible to isolate the influence of the different components which enter into the reaction, such as the silver thiosulphate complex, the type of nuclei, the developer and toners and to study these in detail. The silver grains which are formed can, in addition, be examined by electron microscopy much more easily

than those obtained with the conventional DTR-process, in which the isolation of the grains from the gelatin layer can bring about large deformations in their shape.

6.11.1 EXPERIMENTS IN VITRO. The nuclei: Both silver and silver sulphide nuclei were used. The silver nuclei consisted of a Carey-Lea-sol prepared by reducing silver nitrate with dextrin in the presence of gelatin. Average diameter: 160 Å, specific area: 35 m^2/g.

In some experiments Argyrol (silver nuclei stabilized with the protein vitelline) of the A.C. Barnes Co. was used. Average diameter: 60 Å, specific area: 100 m^2/g.

Silver sulphide nuclei were prepared in gelatin by adding sodium sulphide to silver nitrate. The pAg was adjusted by varying the amount of sulphide. Average diameter: 40 to 70 Å, specific area: 200 to 120 m^2/g.

The solutions:

A: solution of complex silver thiosulphate, prepared from 500 ml of a 0·1 M solution of sodium thiosulphate + 100 ml of a 0·1 M solution of silver nitrate. In some experiments this ratio was changed.

B: Buffer + nuclei + mercapto derivative, containing sodium phosphate 20 g/l, sodium carbonate (anh.) 40 g/l, gelatin (inert): 5 g/l, nuclei 0·47 mg/l of silver, 0·55 mg/l of silver sulphide (in some cases the quantities of nuclei used were 10 to 100 times as large).

The nuclei and the mercapto derivative were mixed $\frac{1}{2}$ hour prior to use. 95 ml of solution B was mixed with 50 ml of solution A and development was started by adding 5 ml of solution C.

C: Standard composition of developer, hydroquinone 16 g/l, Phenidone 1 g/l, sodium sulphite 75 g/l.

Development was carried out at 25° C under continuous agitation. The final concentrations were:

$$
\begin{aligned}
[Ag]_{total} &= 0{\cdot}0055 \text{ mole/l} \\
[S_2O_3]_{total} &= 0{\cdot}0275 \text{ mole/l} \\
[Ag_2S \text{ nuclei}] &= 1{\cdot}4 \times 10^{-6} \text{ mole/l} \\
&\qquad (2{\cdot}5 \times 10^{14} \text{ to } 10^{15} \text{ nuclei/l}) \\
&\qquad \text{to } 1{\cdot}4 \times 10^{-4} \text{ mole/l } (2{\cdot}5 \times 10^{16} \text{ to } 10^{17} \text{ nuclei/l}) \\
[Ag \text{ nuclei}] &= 2{\cdot}8 \times 10^{-6} \text{ mole/l (Carey-Lea: } 1{\cdot}3 \times 10^{13} \text{ nuclei/l)} \\
&\qquad\qquad \text{(Argyrol: } 1{\cdot}3 \times 10^{14} \text{ nuclei/l)} \\
[\text{mercapto derivative}] &= 1 \text{ to } 10 \text{ mg/l} \\
[\text{hydroquinone}] &= 0{\cdot}0048 \text{ mole/l} \\
[\text{Phenidone}] &= 0{\cdot}0002 \text{ mole/l} \\
[Na_2SO_3] &= 0{\cdot}0198 \text{ mole/l}
\end{aligned}
$$

Under these conditions the pAg of the solution was 11·9 and the pH 11·0. The sodium sulphite had no effect on the pAg. The development was stopped

at various stages by adding 1 ml of acetic acid to the reaction mixture. This brought the pH to 4.25.

Transmission spectra were measured in a 2·5 mm cell on a General Electric spectrophotometer (this is a measurement of the total diffuse density). The density was taken as the average of the densities at 400, 450 . . . 700 nm. Reflection spectra were measured in 2 cm cells against a black background (this gave the integral diffuse reflection).

In the study of the kinetics of development the silver was generally determined by chemical analysis. When the silver was so finely divided that it could not be filtered out, the solution was passed through kieselguhr (terra silicea, Merck AG), this adsorbent was then washed until all the silver ions had been removed and the adsorbed silver was then dissolved in nitric acid. The excess nitric acid was then removed by heating in the presence of sulphuric acid and the solution titrated amperometrically with potassium iodide. To make electron micrographs the silver sol was centrifuged, the supernatant liquid decanted and the silver ultrasonically redispersed. When the development has been stopped with acetic acid while it contains excess thiosulphate, further treatment has to be made immediately to prevent corrosion of the silver.

6.11.2 EXPERIMENTS IN EMULSION. For the study of the DTR-process a normal silver chloride emulsion containing 0·95 g of Ag/m^2, was used. The positive contained only gelatin, nuclei and possibly toners. Both negative and positive layers were coated on film.

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VII. APPARATUS FOR PROCESSING DTR MATERIALS

7.1 *General Principles*

Since for the chemical treatment of DTR materials only one processing solution is required, processing is carried out in specially designed apparatus which mainly consists of a tank, two or three leaders which transport the negative and positive separately through the apparatus, and a pair of pressure-rollers.

The prehistory of DTR apparatus may be said to include the model described by Anton Pollak and Friedrich Silberstein (see Appendix, patent No. 1, and Figure 7.1).

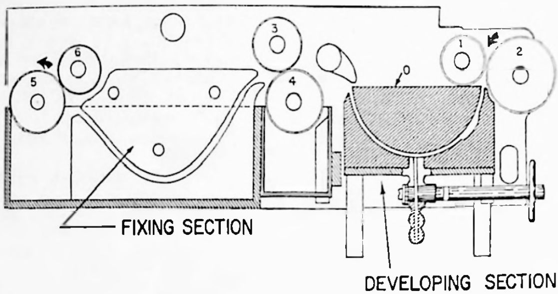

Fig. 7.1. An early developing unit for conventional photographic paper (Pollak and Silberstein) with some of the features later incorporated into DTR apparatus.

This apparatus was intended for use as a developing unit for conventional photographic paper, but was already provided with ribs and pressure rollers placed above each other.

The material is introduced into the developer tank 0 by means of the driving rollers 1 and 2. The pressure-rollers 3 and the leaders 4 advance the material towards the fixing stage. The squeegee rollers 5 and 6 drive the materials to the exit of the apparatus.

The first apparatus for processing DTR materials was described in 1941 by I.G. Farbenindustrie A.G. (see Appendix, patent No. 2 and Figure 7.2).

The negative and positive are introduced separately into the apparatus through the slots A_1 and A_2. The separating element B provides for the moistening of both materials by the developer solution H. By means of an endless belt E and a drum C, the negative and positive are pressed together to form a sandwich. They are transported through the solution until they reach the doctor blade F which leads them outside the apparatus. D1, 2, 3 and 4 are guide rollers for the endless belt.

A more practical model was presented by Walter Eisbein (see Appendix, patent No. 3, and Figure 7.3). This model can be called the prototype of all the modern DTR-apparatus.

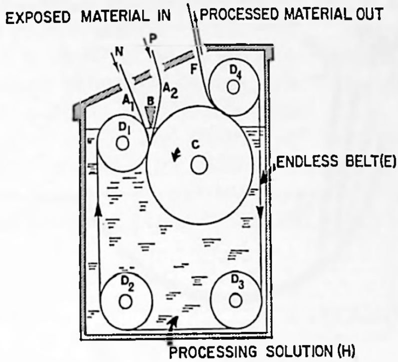

Fig. 7.2. The first apparatus for processing DTR materials (I.G. Farbenindustrie).

The negative and positive are introduced into the apparatus through two or more slots and passed into the processing solution by leaders. Both materials

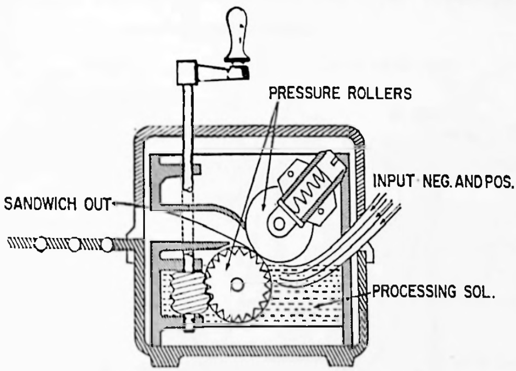

Fig. 7.3. Eisbein's prototype of modern DTR apparatus.

reach the pressure rollers on leaving the solution. These rollers press the negative and positive together to form a "sandwich" which leaves the apparatus in a more or less dry state.

When this system is used both the materials are moistened.

Humphrey D. Murray applied for a patent (see Appendix, patent No. 5) in which a method by which only the positive (stored on a roller) is moistened by

a so-called lick-roller is described. The dry negative (in sheets) is contacted with the positive and both materials are advanced to the pressure rollers.

The quarrel between Walter Eisbein and Marius Böger over patents—which

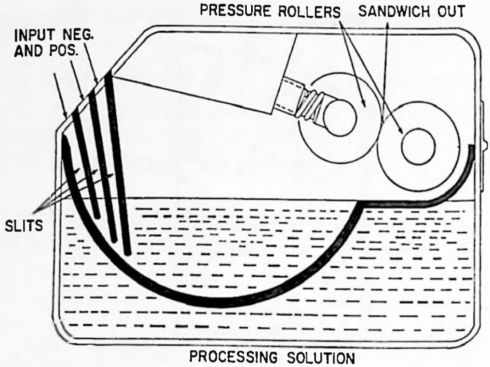

Fig. 7.4. The apparatus marketed by Böger which started his quarrel with Eisbein over patents.

dragged out for years and finally rebounded to the advantage of Eisbein—started when the first apparatus which was described in German patent 969,482 (see Appendix, patent No. 9) and built by Böger was marketed (Figure 7.4).

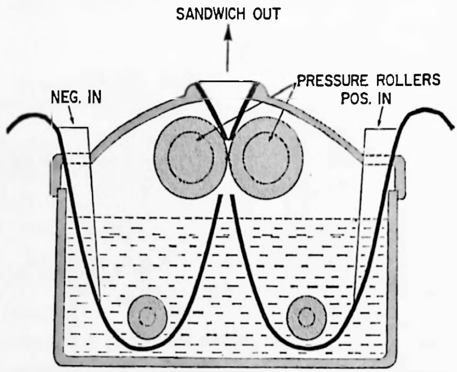

Fig. 7.5. A portable apparatus constructed by Willy Salchow.

The main features of this model are: straight leaders and a curved bottom as a further leader.

By adding one or more compartments to the model described by Eisbein, Willy Salchow constructed a portable apparatus (see Appendix, patent No. 10, and Figure 7.5).

Patents describing a combination of a developing and an exposure unit were applied for by Wolf Stratmann and Walter Limberger (see Appendix, patent Nos. 16 and 21). The Stratmann apparatus is complicated and cumbersome, whereas that of Limberger is efficient and compact and, in a slightly modified form, met with the greatest success.

German patent a.B. 14,567 of M. Böger (see Appendix, patent No. 18) describes the first model having two separate slots through which the negative and positive are introduced in opposite side-walls.

Separate leaders for negative and positive lead both materials towards a pair of pressure rollers situated in the middle of the apparatus.

A completely new conception of apparatus design is the spray installation of Werner Gauditz (see Appendix, patent No. 29, and Figure 7.6).

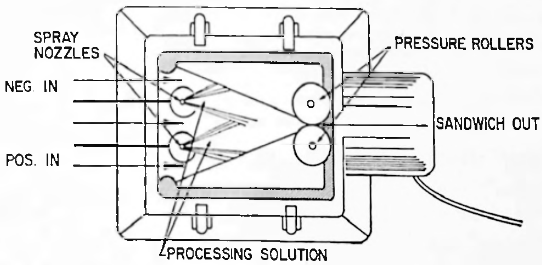

Fig. 7.6. The spray installation introduced by Gauditz.

Leaders separating negative and positive are superfluous as the pressure exerted by the processing solution is sufficient to keep both materials separated until they are seized by the pressure-rollers.

Since a certain amount of processing solution is removed in moistening the sandwich, fresh developer has to be added automatically at regular intervals. This is done, for instance, in the A. B. Dick apparatus, Dutch patent 75070 (see Appendix, patent No. 36) filed by Franz W. Ruys, who describes this arrangement.

When the transfer is carried out on aluminium plates, an additional problem arises, namely that of keeping the negative and aluminium plate in register. Although this problem did not actually arise in 1953, it was already solved in the model described by W. Limberger in German patent 928,213 (see Appendix, patent No. 49) by a pair of rollers which turned upwards. Both the materials and the pressure-rollers lie above the surface of the liquid, thus enabling even the smallest corrections to be made in the relative positions of the two materials.

In 1953 the first patent describing a method for automatically separating the negative and positive was filed by Limberger (see Appendix, patent No. 51).

Other modifications of the methods for leading the materials to the pressure rollers are:

(*a*) the apparatus of the Chemische Fabriek L. van der Grinten (see Appendix, patent No. 68 (which was patented in 1954 and in which the leaders are replaced by a large number of rollers (Figure 7.7).

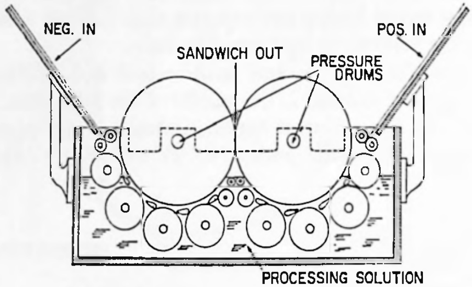

Fig. 7.7. A 1954 apparatus with rollers replacing the leaders.

(*b*) the model which was also described in 1954 by Franz W. Ruys (see Appendix, patent No. 73) and which uses a kind of swing to take hold of one side of the materials and feed them to the pressure rollers where they are then liberated (Figure 7.8).

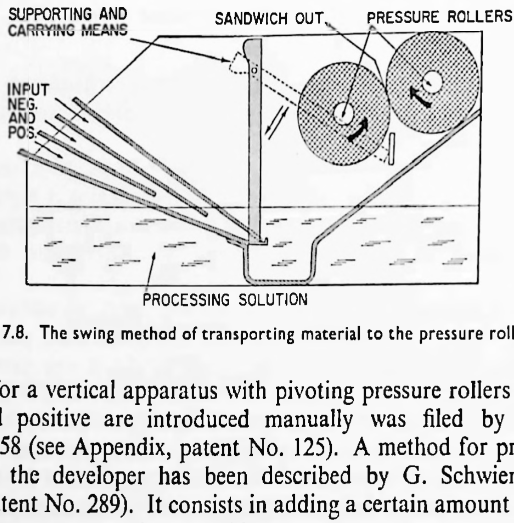

Fig. 7.8. The swing method of transporting material to the pressure rollers.

A patent for a vertical apparatus with pivoting pressure rollers in which the negative and positive are introduced manually was filed by Lumoprint-Zindler in 1958 (see Appendix, patent No. 125). A method for preventing the oxidation of the developer has been described by G. Schwienbacher (see Appendix, patent No. 289). It consists in adding a certain amount of developer solution to the apparatus whenever this becomes necessary.

7.2 *DTR Apparatus for contact copying*

An extremely wide variety of apparatus is available for making contact copies with DTR materials. There is a choice of different models, and each model is made in various formats. They also differ greatly in price, costing from 50 to 650 U.S. Dollars.

This large number can however be reduced to a few basic models. Similarly the contact copying units can be subdivided into three fundamental types:

separate exposure apparatus
separate developing apparatus
combined exposure—and developing apparatus

The first series serves only for exposing the DTR negative materials, the second for processing them. The third series consists of apparatus in which both the preceding types are combined. When it is a question of using DTR materials for copying in offices either an apparatus of the first series and one of the second, or an apparatus of the third series is needed. It is obvious that the copy itself must have the same dimensions as the original.

As far as the exposure-units are concerned, a distinction can be drawn between rotary printers and flat-bed printers. The latter may be subdivided into models for office-copying and models for offset, although both are fundamentally the same. The same distinction can be drawn for the processing apparatus.

One exception can be made: all the different kinds of apparatus which have been placed on the market are of the flowline type.

As regards the exposure unit in combined apparatus, there are apparatus with rotary printers as well as with flat bed printers. In the improved models of rotary printers the DTR materials are advanced through the processing solution and the original is returned to the entry slot. These automatic models may be further subdivided into semi-automatic models or fully-automatic apparatus according to whether or not the processed materials have to be separated manually. The preceding considerations can be summarized as follows:

exposure units	flat-bed printers	for office-copying for small-offset
	rotary printers	for office-copying
processing units	rotary processors	for office-copying for small-offset
	spray processors tank processors	for office-copying for small-offset
combined apparatus	with flat-bed printers	for office-copying for small-offset
	with rotary printers	for office copying
combined automatic apparatus	only with rotary printers	semi-automatic apparatus only for office-copying fully-automatic apparatus (only for office copying)

7.2.1 EXPOSURE UNITS

7.2.1.1 *Flat-bed Printers.* The principle of flat-bed printers dates back to the contact printing frame which has been known from the very early days of photography. The actual exposure-units are in fact only more or less perfected versions of these frames. They generally consist of flat boxes provided with one or more stationary light-sources and a glass support. The original and the sensitive material are brought into intimate contact with each other on the support by means of a pressure device (which is often formed by the cover of the apparatus). The support, which is also called the exposure surface, is translucent, thus permitting the light to act on the light-sensitive material. It is generally made of high-quality glass. The latter is often frosted to give a more equal distribution of light. The thickness of the glass-plate depends on the pressure to which it will be subjected. Moreover it must be smooth and flat.

Intimate contact between the original and the light-sensitive material is of the utmost importance, since two essential characteristics of the copy are greatly dependent on it, namely the sharpness and contrast. One way of achieving this is by making the pressure device more or less elastic by means of felt, foam-plastic, etc.

Another method of obtaining good contact between the original and the emulsion layer is by creating a vacuum between them. By means of an air-pump, the space between the pressure device (a kind of rubber cushion) and the exposure surface can be more or less evacuated so that they are pressed against another, thus avoiding any possible shifting of the original and the negative material and at the same time preventing any light scattering. The use of such pneumatic contact exposing unit is necessary when extremely sharp copies are required, as for example when DTR aluminium offset plates have to be made (see chapter IV).

The light source can be placed above or under the exposure surface; in the case of flat bed printers it is situated under it. It generally consists of one or more incandescent or fluorescent lamps.

Most originals to be copied either have print or writing on both sides, or are opaque, so that exposure has to be made by the contact reflex copying method, in which the negative and the original are arranged in such a way as to make the set-up independent of the opacity of the original. The surface to be copied is placed in contact with the emulsion side of the negative (see Figure 7.9) whilst the back of the latter faces the light source. Before reaching the original, the light passes through the sensitive layer. On reaching the original the rays are either absorbed by the dark areas or reflected towards the photographic emulsion by the light areas. The use of yellow light is recommended with the object of eliminating the short wavelengths which undergo scattering during

reflection, and thus give rise to unsharp images. Other reasons for using yellow light are:

yellow rays penetrate more deeply into the emulsion
the absorption coefficient of the light-sensitive layer is smaller for yellow light than for shorter wavelengths.

The better contrasts thus obtained by the use of yellow light explains why flat-bed printers are generally provided with a yellow filter, a yellow glass plate or yellow coloured light sources.

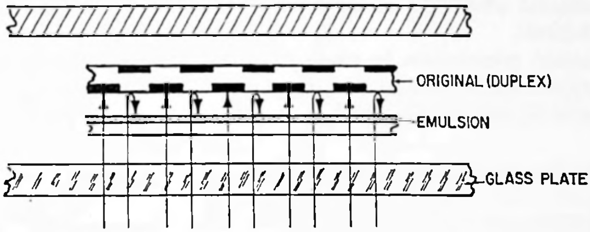

Fig. 7.9. Principle of reflex exposure

7.2.1.2 *Regulation of the Exposure.* Exposure is a quantitative expression of the amount of light acting on the negative material. The exposure (E) is the product of two factors: the light intensity (I) and the exposure time (t):

$$E = I \cdot t$$

Most flat-bed printers are provided with a timer, which is a device for regulating the exposure time:

Since the time of exposure has to be accurately adjusted, the figures on the dial of the timer must be clearly legible and must not be too close to each other. To avoid any waste of photocopying material, the exposure time must be reproducible. Some timers are accurate to 0·1 sec, others to 0·05 sec. The position of the timer on the exposure unit is also important; it must be easily accessible and not get in the way, e.g. when pages in books are being copied.

Some flat-bed printers are provided with a device which enables the exposure to be adjusted by varying the light intensity, the exposure time remaining constant. The intensity of the light is usually varied by means of a rheostat (variable resistance). This method is mostly used when point light-sources are employed.

Flat-bed printers have a larger range of applications than the rotary ones as they can be used for copying all kinds of originals including those which have a very rigid support, such as the pages in books.

The matter of choosing negative materials is not very critical. Most manufacturers of photographic materials furnish several kinds of negative materials differing only in their sensitivity. The Agfa-Gevaert organization has placed three kinds of DTR negative materials for contact copying on the market: Copyrapid Negative Slow (CRS), Copyrapid Negative Medium (CRM) and Copyrapid Negative Normal (CRN).

These three negative materials can be used with most flat-bed printers but the exposure time has to be adjusted accordingly. This allows copying apparatus to be used in offices in which the ambient light is rather bright since in this case a less sensitive material can be used.

An additional advantage of these slow materials is their relatively large exposure latitude.

Only flat-bed printers can be employed when the DTR system is used for special purposes such as making aluminium printing matrices for offset purposes and for the screening work involved in the reproduction of half-tone originals, etc.

From the foregoing it may be concluded that flat-bed printers are much more versatile than rotary ones. It must, however, be borne in mind that a flat-bed printer requires more time and care to manipulate than the rotary ones, since the cover has to be closed down, the timer switched on, the cover opened, in addition to which the vacuum pump has to be operated.

7.2.1.3 *Rotary Printers.* Rotary printers consist mainly of a tubular light source (fluorescent lamp) and a set of rollers and transport belts. The roller

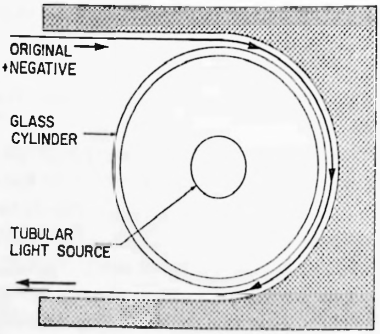

Fig. 7.10. Principles of rotary printers.

system which is driven by a motor, seizes the original and the negative and passes both sheets at constant speed round a cylindrical support placed at a certain distance from the light source (see Figure 7.10). After exposure the original and the negative are again passed out of the apparatus.

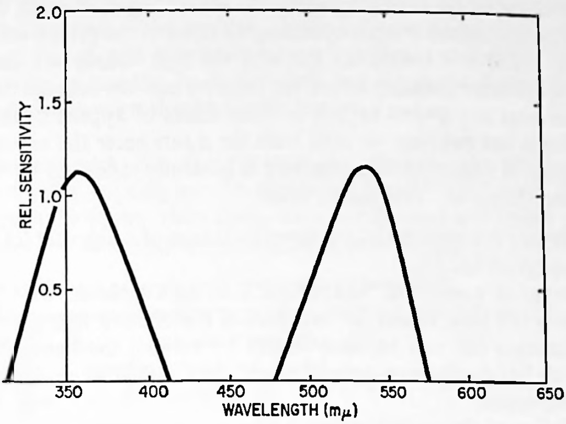

Fig. 7.11. Spectral sensitivity of a negative emulsion for contact copying.

Most ordinary modern rotary printers are provided with a green fluorescent lamp. The maximum in the spectral emission curve of this type of device coincides with a peak in the spectral sensitivity of the material (see Figures 7.11 and 7.12).

7.2.1.4 *Regulation of Exposure.* In rotary printers the lamp and the transport motor are switched on simultaneously. This can be done by means of a

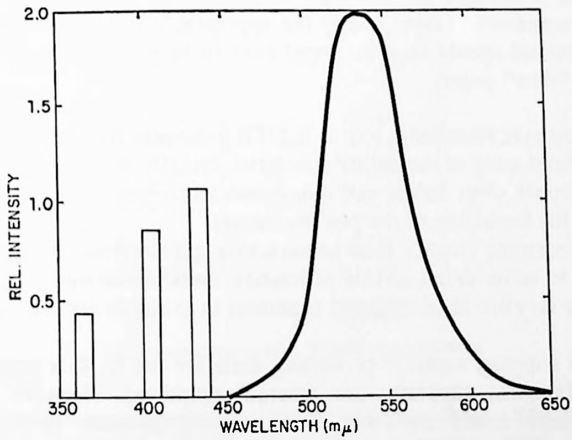

Fig. 7.12. Emission spectrum of green fluorescent tubes.

micro-switch or by the handle by which the plastic bag containing the processing solutions is squeezed or again by closing the cover of the printer (cf. apparatus Lumoprint L 250 and L 400). In this way the light source will have already reached its optimum intensity before the negative and the original pass in front of it. This does not always happen in other kinds of apparatus in which the light source is not switched on until both the sheets enter the exposure-unit.

In the case of rotary printers exposure is generally regulated by varying the illumination (factor I). This can be done:

By varying the intensity of the lamp by means of a rheostat (cf. apparatus Lumoprint LC 25).

By means of a so-called "diaphragm", an adjustable device which partly masks the light source, so that part of the emitted light is intercepted; sometimes this can be done simply by turning the light source itself, which has partly been painted black, thus enabling the dark/light ratio to be varied.

Regulation of the exposure time is also possible but more complicated as this can only be achieved by varying the speed of the transport-motor.

DTR rotary exposure units generally form a part of combined apparatus and are seldom used separately. Their possibilities are not so extensive. They are practically limited to the copying of pages of unbound originals and a vacuum chamber cannot be used: thus the quality of the resulting negative is inferior to that obtained with flat-bed printers. Offset printing matrices on aluminium plates cannot be made with rotary printers.

Their exposure latitude also is less than that of flat-bed printers. In general, a given type is designed for one type of negative only, and not for papers of different sensitivity. Consequently the apparatus which are designed for use with a "normal speed" negative paper have to be put in a darker room than those for "slow" paper.

7.2.2 SEPARATE PROCESSING UNITS. In DTR processors the various stages are as follows: developing of the negative material, transfer of the non-exposed (and non-developed) silver halide salt (converted into complexes), to the positive layer and the formation of the positive image.

In the foregoing chapter their construction, possibilities and qualities were discussed in some detail. Most processing units are driven by means of a motor; the very few hand-operated apparatus in existence are only of historical interest.

In office copying, separate processing units are hardly ever used; for this purpose combined apparatus are generally employed. Separate processing units are used in combination with optical copying methods. They are used for copying on ordinary DTR papers and films as well as for making copies by contact or optically on aluminium plates for offset printing.

Two feeder-slots would normally suffice for separate processing units but there are usually three. This enables "duplex" copies to be made (Duplex-positives are provided with a receptor-layer on each side so that the "duplex" aspect of the original can also be reproduced) It is worth mentioning that only the DTR materials possess this particular feature.

7.2.3 COMBINED APPARATUS. For the most part, the apparatus which are used in the field of DTR copying are the combined ones in which both exposure and developing take place. Here again, there are flat-bed and rotary printers. The reasons for the success of the combined apparatus are:

- The saving in space: only one apparatus is necessary.
- The price of one combined apparatus is less than the sum of the prices of the separate printer and the processing unit.
- The number of manipulations is reduced.
- The manipulations are less complex.

7.2.3.1 *Non-automatic Combined Units.* Most combined apparatus are non-automatic, i.e. after exposure the original must be removed manually and the

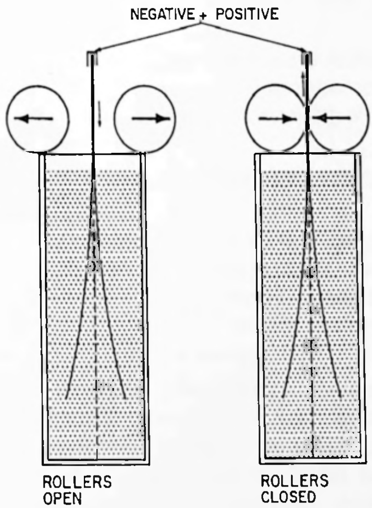

Fig. 7.13. Non-automatic type of combined apparatus.

negative and positive introduced into the processing section. This can be done relatively quickly, but there always remains the two working cycles. The series of non-automatic combined apparatus include the two conventional types of

printers. All the processing units in these apparatus are provided with scales with the exception of the Ravenna processing unit OT 4, an apparatus which is specially designed for offset work. It is provided with a flat-bed printer and a narrow vertical processing tank. In the latter, the negative and the positive are held together with adhesive tape and are introduced vertically. On leaving the processing unit, they are squeezed together by the two pressure rollers in such a way that the aluminium plate is not forced to follow a curved path; this prevents any displacement from taking place in the relative positions of the negative and positive. Moreover, the surface area of the processing liquid which is in contact with the air is greatly reduced. However, the time which elapses between the development of the upper and lower parts of the negative varies and the speed with which the materials pass through the developer solution is not reproducible (Figure 7.13).

7.2.3.2 *Automatic Combined Units.* The two separate working cycles, exposure and developing can be combined into one cycle. In the case of rotary printers, this can be achieved by rejecting the original after exposure and passing the negative and positive through the bath. These are the so-called one-step apparatus.

The latter may be subdivided into:

(1) Apparatus in which the negative and positive must still be separated from each other (semi-automatic instruments).
(2) Apparatus which deliver a finished copy (the fully-automatic ones).

The first series includes the following models:

Lumoprint Bürokopiergeräte LCA (Figure 7.14).
Develop Copymat OT 22 (Figure 7.15).
Fotorapid Electromatic (Figure 7.16).
Swiss Drop Automatic (Figure 7.17).

In the case of fully-automatic apparatus the negative and positive materials are stored on rolls in the machine. The only manipulation required is that of introducing the original into the machine. Moreover the construction of the apparatus is such that the site of installation can be chosen regardless of the ambient light conditions. After the transfer has been carried out, the negative is separated from the positive and again stored on a take-up spool. The positive is automatically cut to the length of the original, just before leaving the apparatus. A number of manufacturers have designed prototypes of fully-automatic DTR-apparatus (Lumoprint, Gevaert Photo-Producten N.V., Develop (Eisbein patent West German patent 1,170,783)).

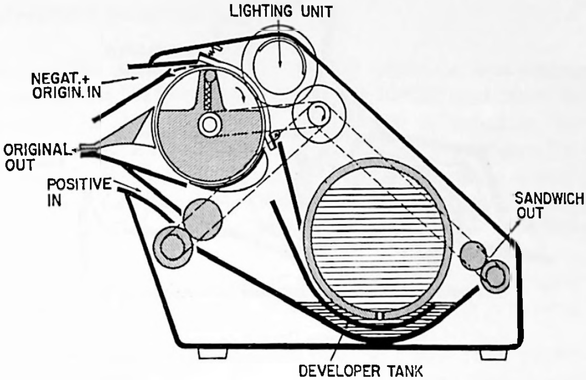

Fig. 7.14. Lumoprint Bürokopiergerate LCA.

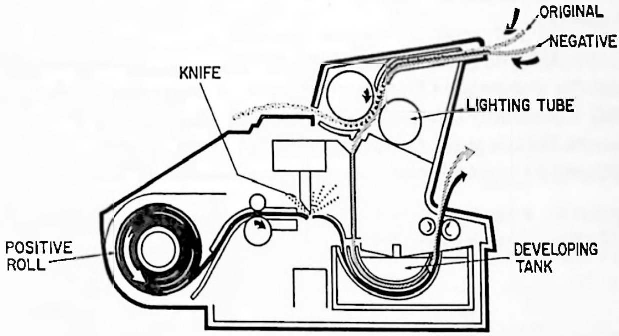

Fig. 7.15. Develop Copymat OT22.

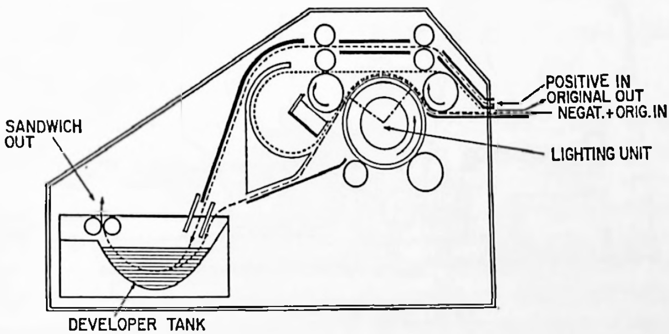

Fig. 7.16. Fotorapid Electromatic.

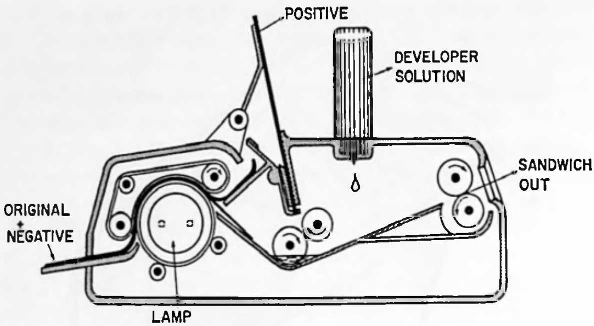

Fig. 7.17. Swiss Drop Automatic.

Only one fully-automatic apparatus has been marketed in the United States. This model is described in German patent 604,557. Five firms sell it under different names:

Transfer-A-Matic (Ozalid Division of Gen. Aniline & Film Corp.)
Transcopy Automatic (Transcopy Inc.).
Photek Consecutor (Photek Inc.).
Centoura Executive (F. G. Ludwig Inc.).
Amptomake (Ampto Inc.)

The apparatus accepts originals of up to 11 inches in width and operates at the rate of about 4 copies per minute (see Figure 7.18).

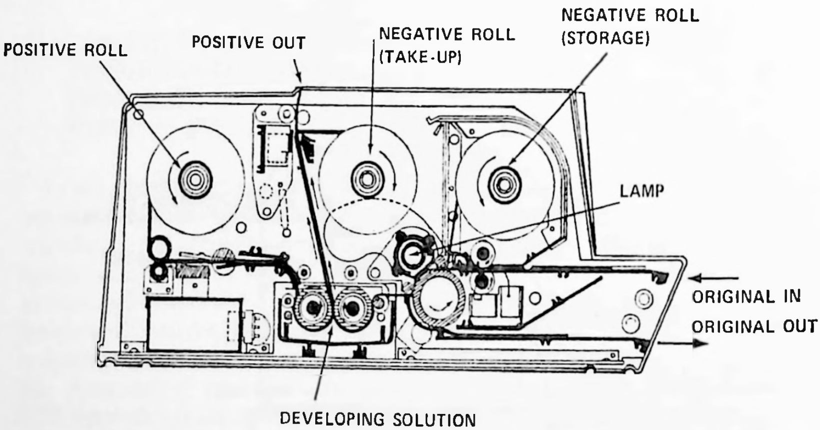

Fig. 7.18. Transfer-A-Matic, which is also sold under other names by various companies.

7.3 *DTR Apparatus for optical copying*

By increasing the sensitivity of the negative materials, thus making optical copying possible, the DTR-system underwent a further expansion; it not only became possible to alter the scale of enlargement or reduction, but contact screening also became easier. The latter was of great importance for the good reproduction of half-tones, so that the system became very useful for offset purposes. Optical copying with DTR-materials, with the exception of one special case, requires two manipulations:

The exposure which takes place in a camera or in a photographic enlarger.
The chemical treatment of the materials in a separate processing unit.

Highly-sensitive negative materials have to be used. These papers can only be developed in bright red darkroom illumination. Not until the negative and positive have been separated may the light be switched on.

7.3.1 PHOTOCOPYING CAMERAS FOR THE DTR SYSTEM. For optical copying with DTR-materials, the cameras do not have to be equipped with a special reversing optical device (mirror or prism). This is not the case when negative and positive layers are coated on a single support (monosheet materials). The usual type of camera gives a laterally-reversed negative, and thus after the image has been transferred to a separate positive a positive which can be read immediately is obtained.

A photocopying camera consists essentially of the following parts: the objective, a negative holder (film plane), a camera-easel (for holding the original) and a light source. The objective consists of a number of lenses all having the same optical axis.

When an objective is used the negative and original are separate from each other, so that the problem of faulty contact between the negative and the original does not arise.

The quality of the objective must be sufficiently high to permit optimum focusing.

7.3.1.1 *The Depth of Field.* One problem in focusing might arise: to obtain optimum sharpness, the camera is focused on the so-called object-plane. In fact, this is the only plane in which the sharpness is the optimum; above and below this plane the sharpness decreases continuously. The region in which the sharpness is still adequate is called the depth of field. Because of the rather long focus of reproduction cameras, their depth of field is relatively limited. With flat, thin originals (e.g. letters) this effect may be neglected, but with thick originals (an open book) problems may often arise, because some of the details lie beyond the depth of field of the lens and are rendered unsharp. This can be

remedied by decreasing the aperture. It may be necessary to rely on the "one-third two thirds" method, which is based on the fact that the depth of field is greater below the object-plane than above it. In practice, focusing is done at about 2/3 of the height of the original when three-dimensional objects are to be reproduced.

7.3.1.2 *The Lens Aperture*. Optimum results are obtained when an average lens aperture is used. The large and small aperture numbers are best avoided. f:22 and f:16 are most currently used. When screening work is being done the main exposure is carried out with a larger aperture (f:8), and the auxiliary exposure is made with a smaller one (f:45).

Modern document copying cameras have a compact vertical structure. A strong tendency to use fully-automatic cameras, is noticeable. With these cameras the determination of the exact exposure time, focusing, etc. is reduced to the minimum.

7.3.2 ENLARGERS. DTR-materials are sometimes exposed in an enlarger. This seldom happens because the originals have to be transparent micro-positives and in practice, such small positives are not always available. Sometimes however it is advantageous first to make a positive by conventional methods and to use this as the original for the DTR-system.

7.3.3 PROCESSING UNITS. Optically-exposed DTR-negatives are practically always processed in a separate processing machine.

7.3.4 COMBINED APPARATUS FOR PREPARING OFFSET-PRINTING MATRICES. As already mentioned, separate exposure and developing apparatus are used for making DTR-offset plates. There is only one exception: there is a so-called "self-contained" machine for producing offset plates: this machine contains both the exposure and the developing units (Fotoplex Camera Processor Model 175—AB Dick Co—built by Robertson). It is a light-tight construction consisting of three main parts:

A storage compartment containing a roll of negative paper (about 350 feet).
The camera itself (objective, camera-easel, timer).
The processing unit in which the negative and the aluminium plate are brought together for further chemical treatment.

The whole has the appearance and the approximate dimensions of an office-desk and poses no particular problems concerning ambient illumination conditions. The machine permits enlarging and reducing between the scales 2/1 and 1/2. It separates the negative from the positive so that it only remains for the aluminium plate to be treated with a preparation to give it its lithographic properties (fixing and lacquering).

7.3.5. APPARATUS FOR MORE THAN ONE PURPOSE. Several manufacturers have designed apparatus combining one or more reprographic systems and the DTR-system. It is clear that in so doing the inconveniences of other systems can be compensated by the versatility which is typical of the DTR-system and which allows high-quality copies to be obtained in conditions in which other systems fail.

7.3.6 COMBINED APPARATUS FOR DTR AND DIAZO. A number of manufacturers produce machines which serve just as well for the processing of DTR-materials as for the processing of diazo-papers and films. The basis of these is as follows: copies on diazo materials can be prepared quickly and economically, especially when more copies of one original are required: apart from non-transparent or duplex-originals, copies on diazo materials cannot however be prepared by the reflex exposure method. They have therefore to be made by means of another system. The DTR-method even allows transparent copies to be made of such originals. These DTR-copies can serve as the positive for diazo-copying.

One of the very first apparatus (in 1953) was the model "Ultramatic" of the "Duplomaster"-series of Duplomat. It was a fully combined apparatus, equipped with two light sources, a high-pressure mercury vapour lamp for exposing the diazo-materials, and a light source adapted for the reflex exposure of the DTR-materials. Both the lamps were built into a rotary printer. A device for processing DTR-materials as well as diazo-materials (with the aid of ammonia-vapour) was also provided. The apparatus allows copies of originals of up to 37 cm in width to be made. The exposure unit in more recent models of these "mixed" apparatus is in the form of a contact printer; the light source consists of a battery of highly actinic white fluorescent or neon tubes for the exposure of the essentially U.V.-sensitive diazo materials.

The same light source can be adapted for the exposure of DTR-materials by inserting a yellow filter between the lamps and the sensitive material. This type of apparatus includes the model F10-Cambi of the firm of Herman Wolff (Luma copy), the NHB-machines of the firm of Castex, the models Mark II, III, IV and V of Fotorapid.

In this type of apparatus the developing unit is seldom separated into two components, i.e. one for the "semi-wet" development of diazo materials and one for the processing of DTR-materials. In other cases the combination "diazo-DTR" is limited to the exposure units. Other recent models have a rotary printer. There is, e.g. a portable apparatus, the Saturn II, manufactured by the firm of Keuffel & Esser: it is provided with a highly actinic selenium-light source for diazo materials which can be adapted for exposing DTR-materials by providing it with a yellow filter. A portable developing box for diazo materials is supplied with this apparatus. The DTR-materials themselves are processed in the built-in developing unit in the apparatus.

Another modification is illustrated by the model Copystar of the Mitta

Industrial Co. (Japan). It is provided with a double light source: a quartz lamp (mercury-vapour 800 W) for exposing diazo materials and a fluorescent lamp (15 W) for exposing DTR-materials. This double light source is reversible: each lamp can be brought into the exposure position.

The exposed diazo material is processed in the apparatus itself (semi-wet method), but for the processing of DTR-materials a separate processing unit is required.

7.3.7 COMBINED APPARATUS FOR DTR AND THERMOGRAPHY. Several manufacturers provide apparatus for making copies by the thermographic as well as by the DTR-method. It is obvious that the imperfections in the thermographic method have been responsible for the design of such apparatus, namely that thermographic methods are not able to copy coloured elements in originals as the ink or dyes used have to be capable of absorbing infra-red light, on the other hand with the DTR process nearly all colours can be reproduced.

A typical apparatus in this series is the model TC 52 of the firm Copid: it combines a rotary printer and an infra-red light source (for the thermographic exposure), a contact frame with conventional light sources (for exposing the DTR-materials) and a device for processing DTR-materials. The apparatus produces cheap thermographic copies as well as high quality DTR-copies.

Another similar apparatus is the model PT of Duplomat. This is also a combined apparatus with an exposure unit in the form of a flat-bed printer which is provided with two kinds of light sources: the usual incandescent lamps for exposing DTR-materials and an infra-red light source for the irradiation of thermographic material. A processing unit for DTR materials is provided (the positive is hardly moistened at all).

7.3.8 OTHER COMBINED APPARATUS. Several manufacturers have designed apparatus for the DTR-systems as well as for the so-called stabilization process (mono- or two-bath process). The apparatus Anken "27" and "12" are adapted for two-bath processing: apart from the developing unit in which DTR materials are processed, a second developing dish in which stabilization processing is carried out is provided. The processor "T9" of "Anken" offers similar possibilities.

By filling the first dish with a special processing liquid which simultaneously develops and stabilizes a material, special materials can then be processed by means of the so-called monobath method.

7.4 *Exposure Problems*

7.4.1 DETERMINATION OF THE CORRECT EXPOSURE. When they have not been pre-exposed, the DTR-negative materials generally reveal relatively large

exposure latitudes. There is a simple method of determining the correct exposure: a series of copies of a contrasty original (dense black text on a white paper) are made, each time using a different quantity of light. When the exposure regulating device is adjusted to the position of short exposure or low light intensity a copy showing very thick characters on a white or a light-grey background is obtained. When, however, it indicates an exposure of long duration or of high light-intensity, very thin, but nevertheless legible characters appear. These two results respectively determine the lower and upper limit of the exposure latitude; the difference between the two exposures will usually be 50% of the smaller one. The correct exposure lies half way between the two limits.

7.4.2 FACTORS INFLUENCING EXPOSURE. A certain number of factors play an important role in the exposure of DTR-negative materials: they are chiefly related to the sensitivity of the latter.

Of the most important parameters the following can be mentioned:

The age of the (non-exposed) negative emulsions: the sensitivity increases by about 3% after storage for one year;

The temperature during the processing. If 20° C is taken as the reference temperature, then the sensitivity will increase by about 6% with an increase of 5° C in temperature. If the temperature rises to 35° C, the sensitivity will increase by 18%.

The temperature during exposure in contact printers. An increase in temperature results in a decrease in the exposure time. Taking 20° C as the reference temperature, the increase in the effective sensitivity is illustrated in the following table:

at 30° C $\pm$ 6%	at 50° C $\pm$ 18%
at 40° C $\pm$ 12%	at 60° C $\pm$ 26%

Any pre-exposure of the negative paper will also increase its sensitivity. It has been proved that a pre-exposure of 10 sec. either to daylight of an intensity of 50 lux or to white fluorescent light of 100 lux results in an increase in sensitivity of about 12%. This effect clearly demonstrates the influence of the illumination of the work room.

The final sensitivity of the materials is also greatly influenced by the kind of positive material used. Thus the relative exposure time of the same negative can fluctuate between + or − 10% depending on the nature of the positive material used.

The exhaustion of the developer also induces an apparent increase in sensitivity, i.e. the greater the exhaustion of the developer the shorter become the exposure times.

Where there is continuous exhaustion of the developer, the sensitivity is

observed to increase with the number of copies made, that of the 10th copy showing an increase of 12% as compared with the 1st copy. From the 10th to the 50th copy the sensitivity again increases by a further 6%, making a total increase of 18%, after which it remains constant.

When the exhaustion takes place discontinuously (e.g. when 10 copies a day are made over a period of 15 days) an analogous phenomenon is observed. The 60th copy shows an increase in sensitivity of 12% as compared with the 1st copy. After the 60th copy the value remains constant. The above-mentioned figures are valid for 1 litre of developer. Such phenomena do not occur with activator-processing: the exposure does not have to be varied.

Certain non-productive influences can also play a role; for example fluctuations in the voltage and in the practical exposure latitude of the apparatus itself.

7.4.3 EXPOSURE CURVE. It is very useful to have some idea of the practical exposure latitude of an exposure apparatus, i.e. the upper and lower limits of its exposure capabilities. This presents no difficulties in the case of flat-bed printers: the minimum coincides with the minimum indication on the timer. There is practically no upper limit: one can expose as long as desired. Excessive exposure times are however to be avoided, because long exposure times can cause over-heating of the glass-plate.

Matters are however, more complicated in the case of rotary printers, in which the exposure is regulated by turning a knob with various subdivisions. With this type of apparatus the exposure latitude is much more limited.

In order to obtain some indication of the exposure latitude of a rotary printer, a so-called exposure curve can be constructed. This is done by means of a transparent step wedge (constant 0·1). For each position of the knob a copy of this wedge is made on DTR-contact negative material. After exposure, the transfer to positive paper is carried out and an image of the step wedge is obtained. After several wedges have been obtained in this way they are pasted on to a piece of paper. A table of wedge-prints is thus obtained. The last still visible areas are now joined together by means of a more or less continuous line. This curve represents the exposure curve, the slope of which gives some idea of the exposure range: the flatter the slope, the smaller is the exposure latitude.

7.4.4 EXPOSURE. The time of exposure (in the case of flat-bed printers) or the exposure device (for rotary printers) must be accurately adjustable. This is of great importance in the reproduction of small details (e.g. the small print in footnotes), where a minor change in the exposure can result in an unusable copy. For originals of this kind the practical exposure latitude is diminished considerably. It is therefore necessary for the exposure to be very easily determined and to be reproducible.

The nature of the original is also of importance: flat originals require a shorter exposure, originals on a coloured background need a longer one.

7.4.5 UNIFORMITY OF THE EXPOSURE. It is very important for the exposure device in an apparatus to be designed in such a way that the light is uniformly spread over the entire exposure surface. The negative materials are in fact very contrasty and this results in a rather large amplification of the local irregularities or fluctuations, leading possibly to a decrease in the legibility of some parts of the copy where it has been either under- or overexposed. Three cases can be distinguished.

7.4.5.1 *Flat-bed Printers.* Flat-bed printers often show a decrease in light intensity towards their edges. This phenomenon is more pronounced at the corners of the exposure surface and thus the negative is seen to have been underexposed in these places, with a resulting loss in legibility.

The uniformity of the illumination can be improved by increasing the number of light sources, banks of lamps generally being used for this purpose. This however poses the problem of the accuracy of their mutual positioning and intensity. A disadvantage of this method is that the entire bank has to be changed if one element fails.

In flat-bed printers which are provided with a vacuum-installation, the uniformity of the light distribution may also be upset by so-called Newton-rings. These are more or less concentric, irregular shaped rainbow-coloured rings which are formed when the contact is "almost good". Air-bubbles are formed between the glass exposure surface and the original, or the negative material, thus giving rise to double reflection at the boundaries and producing an interference pattern due to the local amplification or suppression of the light rays.

7.4.5.2 *Rotary Printers.* In rotary printers, which are generally provided with a fluorescent tube, inequality in the light distribution stems from the light source itself because the latter does not fluoresce uniformly along its axis.

A decrease in the intensity of the light towards the ends of the tube is always observed. This trouble can be overcome in various ways. Firstly by placing a number of black strips on the tube and arranging them in increasing order of number or width towards the centre of the tube where more light is thus intercepted. Secondly by using a specially designed curved diaphragm which has the same effect as the foregoing device. It has also been found very convenient to use a fluourescent lamp of greater length than the maximum width of the apparatus (Lumoprint L 286).

7.4.5.3 *Optical Exposure Units* (*Cameras, Enlargers*). When using copying cameras, it is not sufficient for the light to be distributed evenly over the easel of the camera: it must be distributed uniformly over the exposure surface, i.e. over the back of the camera itself. Allowance must be made for the fact that the intensity of the light decreases non-homogeneously. This decrease is directly

proportional to $\cos^4\alpha$; α being the angle from which the object can be seen. For DTR-materials the decrease must not be allowed to exceed 30 % in order to keep within the limits of the exposure latitude. This requirement is satisfied when the angle α has a maximum value of 25°. This is the reason why only long-focus objectives can be used. Several modern cameras are designed in such a way that the corners of the camera-easel are more fully illuminated than the centre. This has a positive effect on the homogeneity of the distribution of light over the back of the camera.

The intensity of the light which is incident on the camera easel is regulated by varying accurately the distance of the lamps and the angle of their optical axes to the easel. The camera easel is often illuminated by four light sources which are placed symmetrically to it at an angle of 30° to 40°. Another factor which is responsible for inhomogeneous illumination is the effect of stray light. Every possible measure must be taken to avoid this: the camera must be screened from daylight or illumination which has been injudiciously placed in the workroom. The walls of the room in which the camera is situated must not be painted in light colours, any white clothes which the photographers may happen to be wearing may cause undesired reflections.

If a rather small original has to be copied, the white places in the camera-easel must be screened off by means of black paper. The shiny parts of the camera must be painted with a matt paint.

If DTR-materials are used in combination with enlargers (e.g. if micro-positives are available) the same rules hold as for cameras. The baseboard has to be illuminated as uniformly as possible.

7.4.6 CONTACT-COPYING FROM BOOKS. Contact copies of pages can only be made in flat-bed printers. In this case, problems of sharpness arise, especially with the elements along the inner margin. When the books are thick, and strongly bound, some elements may not even be copied at all. In fact it is not easy to press a book open in such a way that the surface of a page can be brought into intimate contact with the negative paper. There are, however, several relatively efficient means of counteracting the loss of contact along the inner margin:

By keeping the book open at as small an angle as possible, of preferably less than 90°. If the angle is obtuse a considerable number of places in the text may be unsharp in the reproduction.

By the use of a strong backing material which is placed behind the page to be reproduced. Such material has to be strong but also thin and flexible: it must reach right up to the margin and follow the curvature of the book.

Another very elegant solution is offered by the use of a so-called book printing pillow.

This is a cushion which is partly filled with air, and which is made of flexible transparent foil. Figure 1 illustrates the way in which it is used: the printing pillow is pressed against the glass of the printer. The negative paper and the page to be copied are placed on top of it. During exposure a light pressure is

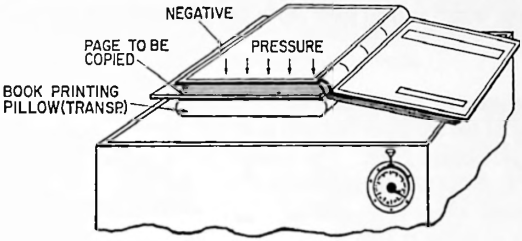

Fig. 7.19. Copying from a book by means of a book-printing pillow.

exerted on the book. The printing pillow should preferably be between 2 and 3 cm. in thickness. The time of exposure, however, has to be increased, as a certain amount of light is diffused. The increase in the time of exposure depends on a number of factors such as the opacity of the foil and the thickness of the pillow: in general allowance must be made for an increase of about 30% to 40% in the times of exposure.

7.5 *Problems of Register in the Case of DTR Offset*

7.5.1 GENERAL. An extremely interesting application of the DTR principle is that of the preparation of aluminium offset printing matrices. It is obvious that this system requires more care to be taken than in ordinary DTR-copying. The image must be in the correct position on the positive material. It is therefore not sufficient for the image to be well-centred and parallel with the edges of the printing matrix, but in the case of continuous printing it is essential for the transfer to be made on the same area and thus reproducibility of the positioning of the positive image presents a big problem, which is generally referred to as "registering" or the alignment of the image on the printing matrix.

7.5.2 ALIGNMENT OF THE IMAGE DURING EXPOSURE—REGISTER SHEETS. In order to obtain relatively "clean" register, care must have already been taken during exposure. There are however, several tricks which enable the image to be placed in the correct position in relation to the negative paper with comparative ease. Contact reflex exposure is facilitated by fixing the original on to a sheet of white paper of the same size as the negative material. During exposure the negative and the backing paper are arranged so that they coincide with each

other. Matters are further simplified by the use of Register sheets. These are sheets of white paper on which a pattern of small squares is printed in a non-actinic colour (generally yellow or light blue). The squares are subdivisions in metric or inch units: the standard paper formats are also indicated on it.

When the exposure is made by means of a camera it is also advisable to use a register sheet, which is then fixed on to the camera easel and the originals are centred on it.

7.5.3 ALIGNMENT OF THE IMAGE DURING TRANSFER. After exposure, the light-sensitive layer of the negative material is brought into contact with the transfer layer of the aluminium plate. The smaller negative paper is centred on the foil. It is now of the utmost importance to prevent the negative paper, which carries the latent image from shifting about on the positive plate: there are several means of doing this.

7.5.3.1 *The Order of Clips.* In order to prevent the negative from shifting about on the positive when the two materials are introduced into the developing unit, they can be fastened together by means of two paper clips, which are attached to the lower left and right sides of the sandwich "paper + plate". Both clips have, of course, to be removed before the materials disappear between the guide members in the apparatus.

7.5.3.2 *Systems with Adjustable Table.* The firm Develop have designed for many of their DTR apparatus a device which permits the aluminium plate and negative paper to be accurately introduced into the developing unit. This device consists of a kind of table which is contructed in such a way that it can be tilted and extended. It is placed at the entrance of the developing unit and may be regarded as a kind of external guide.

7.5.3.3 *Vertical Developing Tank.* The previously mentioned apparatus OT 4 of the firm of Ravenna, with its specially constructed developing- and transfer-unit, permits both the negative paper and the aluminium plate to be correctly and reproducibly placed in the apparatus. The exposed negative is fixed to one of the short sides of the plate by means of transparent tape. The materials are introduced into a vertical developing tank, and, after a certain period, pulled out again. As the path followed by the materials is not curved, no shifting between the materials can occur.

7.5.3.4 *System with a Mobile Leader.* The firm of Photorapid has brought out an alignment system which functions with the aid of a mounting stand and a mobile leader. During exposure the negative and the original are aligned by means of a kind of register sheet. After exposure, the aluminium plate is placed

on the mounting stand: the latter is provided with three rabbet-knobs, two on a long side and one on a short upper side.

The aluminium foil is pushed along until it reaches the axes of the knobs. The exposed negative is then placed on the foil with a long and a short side in contact with the knobs. Both of the active sides are in contact with each other. The negative is fixed to the plate with adhesive tape. The mobile guide is then pushed between the negative and the aluminium plate until it reaches the tape. The whole is then placed in a vertical developing tank.

7.5.3.5 *System with Magnetic Ruler and Tiltable Leader.* In the year 1964, the firm of Duplomat introduced a DTR-offset apparatus, called Rectotransfer. It was especially designed for aligning the image on the plate. The position of the negative on the aluminium plate is fixed before the exposure. This is done by means of a device consisting of a metallic plate and a magnetic ruler. One of the sides of the negative is made to coincide with one of the edges of the aluminium plate, thus enabling even the slightest misalignment either during exposure or during development to be detected. For contact reflex-exposure the original is placed between the negative and the aluminium plate. After exposure, the "sandwich" is introduced between the guide members in the apparatus.

7.5.3.6 *System with Different Trajectories of Negative and Positive.* About 1966, Castex placed their DTR-apparatus OA-10 and OA-20 on the market. This apparatus was designed for achieving great accuracy in the placing of the negative on the aluminium plate, this being done on a table which is situated at the entrance of the apparatus, the materials being brought into register by means of feelers and graduated rulers. The DTR-sandwich is seized by grabber-rollers and forwarded to the developing unit, where both the materials follow different paths but pass through exactly the same distance. On arriving at the high rollers they are joined together again. The development is carried out by means of guide rollers which require very little developing liquid. The developer used for the development is recovered in a plastic bag, thus avoiding any danger of the negative being moistened by exhausted developer solution.

7.5.3.7 *The Eskofot System.* About 1966, Eskofot introduced a combined apparatus called "Planocop Offset", consisting of a vacuum-contact printer and a DTR-processing unit, in which the alignment of the negative in relation to the positive was carried out at the same time. The manipulations are very simple: the use of adhesive tape or clips is not necessary. After exposure of the negative paper, the aluminium plate is placed with one of its short sides against a kind of ruler and with one of its longest sides against a metallic edge. With the aid of a hand wheel, the plate is moved through a constant distance (2 cm) until it makes contact with a second ruler. The exposed negative is

then pushed against the first ruler and aligned against the same edge as the longest side of the plate. By pushing a button, the system "plate + negative" is advanced to the first pair of rollers, thus avoiding any shifting of the two materials in relation to each other.

7.5.3.8 *System with a Non-parallel Input.* The firm of Hoe (U.S.A.) have designed a processing apparatus for DTR offset plates which is especially intended for very large formats and which presents an easy solution to the problem of register. The apparatus which is called Ecan-O-Lith was placed on the market in 1964. An aluminium plate and the negative are introduced into the processing compartment via external guides of stainless steel, which form practically a right angle with each other and have the appearance of two wings projecting out of the apparatus.

The aluminium plate on the right "wing" is placed with its transfer layer face downwards and with one of its long sides against the edge of the guide and one of its shorter sides against a cam, the position of which can be adjusted in relation to the format of the printing machine. The same manipulations are carried out with the exposed negative on the other "wing". The light-sensitive emulsion layer is also turned face downwards.

The machine is started up by pressing a button and both sheets proceed towards the developing solution. On leaving the latter they come together, layer against layer, and are squeezed by two rollers. The speed of the processing can be varied by means of an electric motor.

7.5.3.9 *Miscellaneous.* It is impossible to give a complete survey of all the solutions which have been put forward for solving the problem of registering. The aim of the foregoing paragraphs was just to mention the methods which are currently employed and which have been successfully placed on the market. A number of other firms have tried to present other solutions, but the inventive value or the use of the latter was generally found to be either too complicated or was limited to one particular apparatus.

The number of patent applications (see end of chapter "Apparatus") clearly demonstrate the importance which was and still is attached to the problem of "clean" register and the large variety of solutions which have been put forward to solve it.

7.6 *Processing Apparatus and Processing Liquids*

A discussion of some of the problems which may arise in the use of processing solutions in DTR apparatus may be of some interest.

7.6.1 DISH DEVELOPMENT. DTR materials require only one processing solution. This liquid was called a "developer" right at the beginning of the

DTR process. In the apparatus of those days this developer was placed in a developing dish into which the negative and positive were guided by guide members and brought together. This initiated the complicated physico-chemical process which resulted in the production of a positive. The DTR developer had however some of the disadvantages of most photographic developers: it was a rather strongly alkaline solution, forming easily oxidizable compounds: moreover a large surface was exposed to the air and thus the surface/volume ratio was rather large. Oxidation took place when the developer was being used as well as when it was not in use.

When only a few copies had to be made each day this meant that the activity of the processing solution decreased rapidly solely on account of atmospheric oxidation.

This oxidation was partly prevented by returning the developer to a bottle at the end of the day, thus greatly reducing the surface which was exposed to the air.

7.6.2 DEVELOPER IN A PLASTIC BAG. The surface in contact with the air was greatly reduced by keeping the processing solution in plastic bags when the apparatus was not in use. The bag-system was introduced in 1958.

Nowadays, most apparatus are provided with it. When the apparatus is to be used, the developer solution is squeezed towards the processing dish by means of a handle or a pump (the bag and dish are connected with each other by means of a plastic tube).

Thus the processing solution is, practically speaking, no longer in contact with the air; moreover not only the oxidation, but also the evaporation of the developer are greatly reduced.

The advantages of the bag-system are as follows:

1. The life of the processing solution is increased so that more copies can be made with the same volume of developing solution.
2. The manipulations involved in renewing the processing solution or cleaning the apparatus are simplified. There is no longer any need to pour the solution out of the dish into bottles at the end of each day.

Nowadays there is a strong tendency to use so-called activator solutions instead of a developer, although the use of the bag-system still remains popular. Whereas the oxidation of the developer has no longer to be taken into account, the problem of evaporation, however, still remains. However, crystallization of the dissolved ingredients is counteracted.

Recent models are designed in such a way that liquid has to be present in the dish before copying can be commenced. A further improvement in the apparatus is the incorporation of a magnetic device which guides the liquid towards the dish and returns it automatically into the bags at the end of the operation (e.g. the model Printa Matic manufactured by Duplomat).

7.6.3 OTHER SYSTEMS. A large number of other apparatus (which in one or other way are related to DTR processing) have been the subject of patent claims.

7.6.3.1 *Systems with an Invertible Flask.* As long ago as 1957 the firm Focoop introduced the so-called chicken-feed system (see Figure 7.20), the principle of which is to keep the processing solution in an invertible plastic flask, which is connected with the developing dish by placing the flask upside down. The apparatus is made ready for use (developer solution flows into the dish). After copying, the flask is again inverted and the liquid returns to the bottle. The

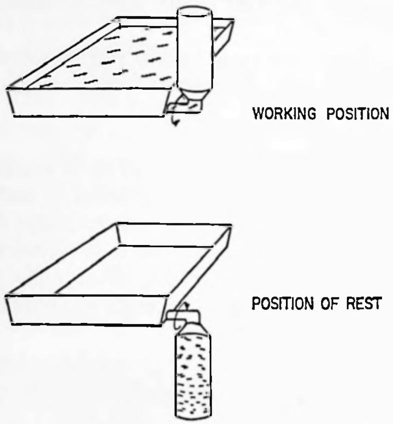

Fig. 7.20. Chicken-feed system of filling and emptying developing dish.

object of this sytem is to reduce oxidation of the developer to a minimum and to cut down the number of manipulations.

To replenish the liquid, the flask is unscrewed and the exhausted developer thrown away. The developing dish is then filled with fresh solution and the empty flask is again fixed into position. The cleaning of the developing dish thus becomes a very simple matter.

The level in the dish is kept constant irrespective of the number of copies which are produced.

7.6.3.2 *Spraying Installations.* Another special device is the so-called spraying installation. In this type of apparatus, the materials are not immersed in the solution, but only their surfaces are moistened with developer solution. This device is employed in the Spray-O-Matic system, which was introduced in 1960 by Duplomat. In this type of apparatus the liquid is pumped automatically and in an air-tight manner as long as the apparatus is in the "Stand by"

position. A built-in electromagnetic valve pushes the liquid from the relatively big reservoir in between the active layers of the two materials. On starting up the apparatus the oxidation developer circuit is automatically put into operation. The great advantages of this system are that the DTR processing takes place more rapidly and oxidation and the consumption of developer are reduced to the very minimum, and moreover the apparatus is very compact.

7.6.3.3 *Systems with the Developer in a Closed Circuit.* To avoid the daily filling and emptying of the developer tank, in 1959 the firm of Bogiphot introduced an apparatus with a so-called "developer pump". In this apparatus, by pressing a button, the developer is pumped from a reservoir towards the developer device and by pressing a second button the liquid is returned to the reservoir. The latter is thermostatically controlled to maintain the optimum processing temperature (19–22° C) and thus in winter (even in poorly-heated rooms) good copies are still obtained.

The firm of Kohler employs the system of pumping in a closed circuit to avoid unnecessary manipulations and having continually to replenish the plastic bags with developer.

7.7 *Auxiliary Apparatus for the DTR System*

7.7.1 GENERAL. Apart from essential apparatus such as printers, cameras and processing apparatus, there are also very many auxiliary apparatus which are used in DTR copying. Of these, for instance, paper cassettes, drying-frames, drying-apparatus, devices for the automatic filling of the dishes, filing cabinets, etc. can be mentioned. In designing such apparatus, much attention has been paid to the function and compactness of this equipment.

7.7.1.1 *Paper Cassettes.* To avoid having to remove a sheet of positive and negative paper from their respective packages each time a copy had to be made and always having to make sure that the package containing the negative papers had been closed in a light-tight manner so as to prevent any possibility of pre-exposure, so-called paper cassettes were created. There are models for negative (light-tight) and for positive materials and combined models with two compartments. Sometimes a supplementary compartment for storing the originals is also provided. The cassettes are generally designed for the storage of 100 sheets.

On pulling a handle, a sheet of paper is ejected. Paper cassettes can usually store only one size of paper, although there are some models which can be adapted to take two or three formats.

7.7.1.2 *Drying Apparatus.* Small drying frames are very suitable for subjecting copies which have not been made by the DTR "dry" method to a short

period of drying. They consist of a number of tiltable grids which are placed one above the other. The copies no longer have to be spread out on a table for drying; such frames always provide sufficient ventilation.

These frames may even be used as a kind of small sorting-table. Most of them are provided with a thin layer of plastic which prevents them from rusting. After drying, the grids are folded together, so that the apparatus takes up only a small amount of space. There are several models which can be attached to the wall.

There are also more complicated drying apparatus which are generally provided with infra-red sources and a thermostat. Some models have a wire-shaped grid in the form of an endless belt on to which the copies are laid. This enables a large number of copies to be dried very quickly. However, such apparatus is declining in importance owing to the ever-increasing use of the "dry" method of copying.

A modification of the above-described frame is a rack for storing DTR aluminium offset matrices in separate compartments. This avoids any damage which might otherwise be caused to these master copies by placing them on top of one another. Moreover, it is inefficient to stack the aluminium plates in this way, because the "images" are not immediately visible and therefore, in order to find a given plate, the entire pile has to be examined.

7.7.1.3 *Filing Furniture.* Some firms market furniture which is designed for office copying purposes. It consists of various models of cases, with a wide variety of applications and having the appearance of a desk, so that they do not look out of place in an office. The DTR apparatus is placed on a case of this kind which contains compartments for the storage of materials, paper cassettes and chemicals. Some models even have a slot through which the processed negative is thrown into the case.

Other models have the appearance of a working-table, so that work can be done while seated. There is, for instance, a model which is provided with a reservoir of large capacity which is connected to the apparatus by means of a pump and which only needs to be refilled at infrequent intervals.

7.7.1.4 *Automatic Filling and Emptying Apparatus.* These generally consist of a plastic bottle of relatively large capacity, provided with a pump or siphon which permits the dish in the DTR apparatus to be filled and emptied quickly and easily.

7.7.1.5 *Fixing Plates.* Fixing plates are used during the supplementary treatment (fixing, lacquering and correction, if necessary) of DTR-aluminium offset matrices. They are generally smooth and flat supports to which an aluminium plate can be attached by means of a clip. The plates are usually made of a plank coated with plastic board, and can be easily washed.

CHRONOLOGICAL LIST OF IMPORTANT PATENTS AND PATENT APPLICATIONS

1. German Patent 152,770—13.5.1902—Vereinigte Elektrizitäts A.G.
   Pollak
   Silberstein
   Photographic material, driven by pairs of rollers, passes through guide slots into a developing and fixing section and is conveyed through it.
   See also part 7—Chapter 1—reference 1.
2. French Patent 879,995—24.1.1941—I.G. Farbenindustrie A.G.
   6.2.1941
   6.3.1941
   The negative and positive material are introduced separately into the liquid and are transported in the form of a sandwich, between a roller and an endless belt, out of the apparatus.
   See also Part 7—Chapter 1—reference 2.
3. German Patent 802,369—13.5.1949—W. Eisbein
   From an opening located above the liquid two or more curved parallel guide elements move the materials through the liquid to two pressure rollers rotating against each other.
   See also Part 7—Chapter 1—reference 3.
4. German Patent 804,890—13.6.1949—W. Eisbein
   Double guide walls according to German Patent 802,369 (3) guide the materials separately through the liquid to a pair of rotating pressure rollers to reach a separating device where a doctor blade prevents the moistened papers from adhering to the rollers.
5. United Kingdom Patent 713,163—13.7.1949—Ozalid Comp. Ltd.
   The positive paper in roll form is moistened with developing liquid by means of a lick roller, is thereupon contacted with a sheet of negative paper and both contacting papers are then conveyed between two pressure rollers.
   See also Part 7—Chapter 1—reference 4.
6. German Patent Application B 2301—27.2.1950—Dr. Böger K.G.
   Very long guide members. The sheets do not contact each other until they emerge from the liquid.
7. German Patent 828,481—4.4.1950—W. Eisbein
   The positive paper moves in a separate dry intermediate channel, the apertures of which are situated above the liquid. Above and beneath this channel guide members are positioned for guiding one or two negative paper(s) through the liquid to the pressure rollers. After the materials have been peeled apart, the positive paper is left almost dry.
8. Swiss Patent 285,164—14.4.1950—W. Graf
   The exposed negative is attached with its back surface to a cylinder and is transported in this way through the developing liquid. On leaving the liquid the negative and the positive are pressed together and the sandwich thus formed is almost dry when it leaves the pressure rollers.
9. German Patent 969,482—2.5.1950—Dr. Böger K.G.
   Straight guide members guide the materials into separate positions below the level of the liquid. In passing over the curved bottom part of the apparatus the two materials are brought into contact with each other and are guided to a pair of pressure rollers.
   See also Part 7—Chapter 1—reference 5.
10. German Patent 843,362—23.6.1950—W. Salchow
    Positioning of the guide members according to German Patent 802,369 (3). This apparatus, however, contains several sections in which the liquid can be stored thus making it possible to transport the apparatus.
    See also Part 7—Chapter 1—reference 6.
11. German Patent 856,845—12.7.1950—Fotokopist G.m.b.H.
    Both materials are stored in roll form. The negative is cut off before it is gripped by the inlet rollers, is then passed through the liquid and emerges above the level of the liquid while it is still in contact with the positive. On leaving the pressure rollers the positive is also cut off. A feeler element in the form of a roller ensures the synchronous transport of both materials.
12. United Kingdom Patent 699,085—14.7.1950—Ozalid Comp. Ltd.
    Positive or negative material are moistened by a lick roller while the other material is conveyed in a dry state to the pressure rollers.

13. German Patent 856.844—24.8.1950—W. Eisbein
Addition to German Patent 802,369 (3).
Wires are tensioned between the guide members and the exterior wall of the apparatus and while resting in the grooves of the pressure rollers these wires prevent the material sandwich from rotating together with these rollers.
14. German Patent Application B 13,193—27.12.1950—Dr. Böger K.G.
Guide members and guide rollers convey the materials separately through a considerable distance and in such a way that the formation of bubbles is avoided.
15. German Patent 848,013—5.3.1951—Fotokopist G.m.b.H.
The positive material containing a solvent for the silver halide and the negative run in separate channels which are independent of each other.
16. German Patent 847,846—24.3.1951—W. Stratmann
Both materials in roll form are cut off after the exposure of the negative and are conveyed to the tank by means of rollers and endless belts. In the tank, the positive material passes through a liquid which contains a silver halide solvent while the negative is passed through a developing bath. After transport between the pressure rollers both materials are heated so that drying takes place within a short time.
See also Part 7—Chapter 1—reference 7.
17. German Patent 847 845—27.3.1951—Fotokopist G.m.b.H.
After the exposure of the negative paper in roll form it is rolled up together with the positive paper which is also in the form of a roll, with the coated layers of each material in contact. After a definite number of exposures the roll is then developed.
18. German Patent Application B 14,567—14.4.1951—Dr. Böger K.G.
One guide member for the negative material and one guide member for the positive material extend from the two opposite sides in the apparatus and join up in the middle of the apparatus at a point slightly above the liquid, and right under the pressure rollers. A guide roller is provided for each guide member.
See also Part 7—Chapter 1—reference 9.
19. German Patent 853,262—16.4.1951—W. Stratmann
The negative, which is driven by several pairs of rollers, is conveyed through the liquid. The positive which is driven by rollers and endless belts, follows another path, so that it joins, in a dry state, the moistened negative at a point right in front of the pressure rollers.
20. German Patent 856,846—4.5.1951—Fotokopist G.m.b.H.
The negative and positive material in roll form travel over guide rollers through different tanks which either do or do not contain the same liquid. After they have been pressed into contact, they travel together for a time whereupon they are finally separated and rolled up.
21. German Patent 968,956—19.6.1951—Lumoprint-Zindler K.G. Apparatus combining the exposure part and the processing tank in one and the same unit. The negative and positive materials, each in the form of rolls, are cut into sheets shortly after they have left the feed rolls. The original and the negative material pass together in front of a cylindrical lamp.
See also Part 7—Chapter 1—reference 8.
22. German Patent Application D 10,238—2.9.1951—Dokuphot Apparatebau
Developing apparatus for diffusion transfer materials according to (9). The partitions are provided with teeth. Scrapers or endless belts not only prevent the materials from rotating together with the rollers, but also transport the materials out of the apparatus.
23. German Patent Application B 16,897—24.9.1951—Dr. Böger K.G.
At the extremities of the rollers resilient belts which provide for the necessary pressure are arranged.
24. German Patent 966,736—17.11.1951—Schneto A.G.
Guide members which are curved in different ways make each of the materials follow a different path and in such a way that the difference in the distance due to the curved bottom part is neutralized.
25. German Utility Model 1,638,730—5.12.1951—Dr. Böger K.G.
A drive mechanism and a tank containing the liquid are mounted next to each other on a base plate. The drive mechanism contains a transformer, a rectifier and a motor.
26. German Patent Application B 18,226—17.12.1951—Dr. Böger K.G.
The negative and the positive material—separated from each other—are gripped along opposite sides by *two* inlet rollers and are moved towards each other by means of guide members which are situated below the level of the liquid. Pressure rollers convey the sandwich of negative and positive out of the apparatus.
One of the inlet rollers also functions as a pressure roller so that two pairs of rollers are sufficient.

27. Swiss Patent 296,696—12.12.1951—E. Kohler
Besides a developing tank with guide members, a rinsing tank in which the heated material containing the treated images can be submitted to an after-treatment is also provided. It is only necessary to interchange the tanks. The rinsed sheet is then squeezed dry by the same pair of pressure rollers. This rinsing tank may also be used for developing diazo materials.
28. German Patent 890,455—31.12.1951—Dr. Böger K.G.
The lens system and the shutter provide for the correct exposure of the negative in roll form After the negative material has been cut off it joins the positive material which is also cut off; both materials travel then together through the processing bath.
The heat emitted by the lamps during exposure provides for the drying of the materials.
29. German Patent Application K 12,825—12.1.1952, Kontophot-Wedekind K.G.
Non-conventional method.
The negative and the positive materials are not immersed but are moistened by a spray system. The customary guide members are not necessary since the liquid keeps the materials apart until the moment when they are gripped by the pressure rollers.
See also Part 7—Chapter 1—reference 10.
30. United States Patent 2,742,838—16.2.1952—General Photo Manufacture Co.
Developing apparatus which can be compared with (3) with the addition of some improvements, which are already known such as: a guide roller, pressure adjustment of the pressure rollers, a doctor blade on these rollers and valves used for filling and emptying.
31. Dutch Patent 78,805—1.4.1952—Van der Grinten N.V.
Apparatus for treating materials by the OCE-TRANSFER process.
This embodiment also enables diffusion transfer materials to be treated. One of the two materials is kept dry whilst the emulsion on the other material is moistened by a lick roller. The customary pressure rollers press the two materials together.
32. German Patent Application F 8,995—6.5.1952—Agfa A.G.
Instead of pressure rollers a pressure plate is provided. This pressure plate permits the relating positions of the papers to be altered after they have been immersed. Incorrectly positioned prints and creases are thereby avoided.
33. German Utility Model 1,641,648—8.5.1952—Agfa A.G.
Non-curved guide members guide the negative and positive material separately from each other, to beneath the level of the liquid where they are gripped between a pressure roller and a rotating drum which carry the materials out of the apparatus. A stationary guide member is fitted around the drum.
34. German Utility Model 1,641,703—8.5.1952—Agfa A.G.
Apparatus similar to (33). Here the stationary guide member fitted around the drum is replaced by an endless belt.
35. German Patent 973,400—8.5.1952—Agfa A.G.
Rotating drum, which is situated partly in the developing liquid and which moistens one of the materials only on one side, while the other sheet of material is transported through the liquid. Both materials meet each other at a point immediately in front of the two pressure rollers.
36. Dutch Patent 75,070—7.6.1952—A. B. Dick (Holland) N.V.
9.1.1953
A bottle containing a supply of developing liquid which can be placed in two positions. When the bottle is turned upside down the developing tank becomes filled to a definite level, the tank is also replenished by means of this bottle. When the bottle is turned downwards the liquid flows back again from the tank into the supply bottle.
See also Part 7—Chapter 1—reference 11.
37. Swiss Patent 306,080—22.8.1952—Forschungsinstitut Zürich
Exposure and developing apparatus with an adjustable resistance to regulate the light intensity, a heating element with a thermostat for the developer and a pouring out element for emptying. The light source (a tubular lamp) is surrounded by a housing which allows a greater quantity of light to be transmitted towards the extremities since the intensity of the light transmitted by the lamp is less in that area.
38. Swiss Patent 305,441—22.8.1952—Forschungsinstitut Zürich
Exposing and developing apparatus.
The lower guide member serves as a bottom and has an area in which impurities are collected. The small exposure lamps do not heat the paper.
39. German Patent 918,372—25.8.1952—W. Eisbein
Obliquely positioned pressure rollers.
40. Austrian Patent 179,710—25.8.1952—Lumoprint-Zindler K.G.
The pressure rollers are pressed against each other by means of metal springs.

41. German Patent 1,003,580—1.9.1952—Agfa A.G.
Developing apparatus for diffusion transfer combined with a drying drum. An embodiment without pressure rollers is also described, but has not been mentioned in the claims.
42. German Utility Model 1,647,295—11.9.1952—Dr. Böger K.G.
The pressure rollers are pressed against each other by means of a resilient belt.
43. German Patent 932,474—26.9.1952—W. Eisbein
In order to prevent the sandwich from rotating together with the pressure rollers, these rollers are provided with slots in which a scraper is positioned.
44. Dutch Patent Application 172, 994—8.10.1952—F. W. Ruys
Apparatus according to (3) with, however, the difference that the guide members and/or the rollers can each be removed separately.
45. German Patent 1,059,286—8.10.1952—Lumoprint-Zindler K.G.
A negative and a positive material each follow a separate path, are moistened by means of a lick roller. The two materials meet each other at a locus in front of the pressure rollers. Vertical construction.
46. Dutch Patent Application 174,580—13.12.1952—F. W. Ruys
The pressure rollers are arranged at different heights, the back roller being placed in a higher position than the cooperating front roller.
47. Swiss Patent 322,288—9.1.1953—Focoop N.V.
Rotatable liquid container which is vertically adjustable and is connected with at least one opening in the developing tank.
48. German Patent 926,175—22.1.1953—Agfa A.G.
The negative coated on to a thin support is temporarily attached to an auxiliary support; this set, together with the positive, is transported through the developing tank.
49. German Patent 928,213—3.2.1953—Lumoprint-Zindler K.G.
Pressure rollers which can be raised above the level of the liquid enable the negative and positive materials to be placed between the rollers in a correct position while in the dry state. When the pressure rollers are snapped back into the downward position, the negative and the positive material become immersed in the liquid.
(See also Part 7, Chapter 1, reference 12.)
50. German Patent 959,614—3.2.1953—Lumoprint-Zindler K.G.
Developing apparatus which can be used in practice for the diffusion transfer reversal process as well as for the fixing development process. Various embodiments are possible. All of them have, however, only one pair of pressure rollers for both the processes.
51. German Patent 965,839—6.2.1953—Lumoprint-Zindler K.G.
Behind the pressure rollers the sandwiched materials are transported between two endless belts towards a faster rotating pair of rollers, which together with a separating member separate the negative from the positive material.
See also Part 7—Chapter 1—reference 13.
52. French Patent 1,081,179—23.4.1953—F. Ecal
The exposure unit and the developing apparatus together form a single apparatus. The lid of the developing apparatus serves also as the bottom part of the exposure unit.
53. German Patent 1,039,829—25.4.1953—Lumoprint-Zindler K.G.
Optical printing process in which the sizes can be modified and in which the original and the negative are moved in opposite directions during the exposure. The developing apparatus is also suitable for the diffusion transfer reversal process. The materials are cut off and also dried.
54. United Kingdom Patent 759,714—8.5.1953—Van der Grinten N.V.
Apparatus for the OCE-transfer system which comprises a horizontally located pair of rollers, at least one roller of this pair rotating in a liquid. Endless belts convey the materials between the pressure rollers. This apparatus can also be used for the diffusion transfer reversal process.
55. United Kingdom Patent 761,602—8.5.1953—Van der Grinten N.V.
Applies to the same system as 54.
The endless belts are however replaced by a clamping device.
56. French Patent 1,098,021—28.5.1953—F. Ecal
The exposure unit is located above the developing device; together they form one apparatus. The lid of the developing device serves also as the bottom of the exposure unit. This apparatus can be used for various light-sensitive systems (e.g. for diazo). A number of guide members allow one of the materials to be conveyed in a dry state to the pressure rollers (compare with 52).
57. United Kingdom Patent 752,403—3.6.1953—Van der Grinten N.V.
A diffusion transfer reversal process OCE-transfer) wherein at least one of the materials is moistened, and both materials are brought together and conveyed between an upper and a lower pressure member. These pressure members can be moved in relation to each other; the pressing surface of the lower member consists of a hard porous material whereas the pressing surface of the upper member consists of a resilient material.

58. United States Patent 2,786,401—11.6.1953—American Photocopy Equipment Comp.
In order to prevent the products of oxidization from depositing on the guide members and in this way soiling the support, use is made of thin guide members.
59. Dutch Patent 82,809—30.6.1953—Van der Grinten N.V.
Transfer apparatus for the combined steps of moistening and pressing the materials on to each other. This apparatus can, if required, be used for the diffusion transfer reversal process.
60. Swiss Patent 316,178—9.9.1953—Büro-Geräte A.G.
Especially curved guide members make the negative and the positive cover the same distance.
61. United States Patent 2,792,768—5.10.1953—Ludwig
A simple, portable and cheap apparatus. The pressure rollers are made of foamed rubber. The outer rim is made of a Latex material so that the products of oxidation cannot penetrate into the pores. Collapsible (foldable) guide members are positioned, each in opposite side walls. The negative and positive materials are conveyed into the tank. Round guide members located in the liquid guide both the materials to the pressure rollers.
62. Swiss Patent 320,781—23.10.1953—Wiss. Forschungs-institut, Zürich.
Developing apparatus for the diffusion transfer reversal process is housed together with two exposure units in one arrangement. (Intended for letters and books.)
63. German Patent 1,034,025—28.10.1953—Dr. Böger K.G.
Straight guide members guide the negative and the positive material to a pair of pressure rollers which are located under these guide members and under the level of the liquid. The sheets are in contact with the developing solution for only a short time and thus absorb but little liquid. A curved guide member conveys the sandwich to a second pair of pressure rollers which is located above the liquid. Both pairs of rollers are driven synchronously.
64. Swiss Patent 315,341—29.10.1953—Büro-Geräte A.G.
Apparatus comprising an independent tank with inlet guide members, pressure rollers and a bottom part which serves also as a guide member. A special coupling between the pair of rollers and the motor enables the tank to be removed from the apparatus.
65. French Patent 65,478/1,081,179—5.11.1953—F. Ecal
In order to counteract the oxidation of the developing solution the latter is stored in an air-tight supply container. Only a small quantity of the developing solution is contained in the actual developing tank. The developing solution is fed automatically and is arrested by a floating system as soon as the required level has been reached.
66. Swiss Patent 325,857—11.1.1954—Agfa A.G.
Guide members guide the material through the developing solution to a set of three rollers, an endless belt passing between the function of these members is to press the materials together and to transport them out of the apparatus.
67. German Patent 1,029,232—22.1.1954—Agfa A.G.
The negative and the positive material are each conveyed by an endless belt into the developing solution. At the point where both materials meet, they are pressed together by means of pressure rollers. The endless belts carry the sandwich of the two materials through the liquid out of the apparatus (improvement of 48).
68. Dutch Patent 85,131—27.1.1954—Van der Grinten N.V.
The curved guide members are replaced by a large number of rollers.
See also Part 7—Chapter 2—reference 14.
69. Dutch Patent Application 184,859—4.2.1954—F. W. Ruys
A cylinder provided with an element for gripping the negative and positive materials rotates in the developing solution, and both the materials are transported through the developer by means of this gripping system. The gripping system becomes inoperative as soon as the materials are gripped by the pressure rollers.
70. German Utility Model 1,675,910—10.2.1954—Büro-Geräte A.G. Zürich
Apparatus combining an exposure and a developing unit. The exposure unit is situated under the apparatus and comprises lamps and a stationary sheet of ground glass against which a resilient pressure system presses the document to be copied (e.g. a book).
The developing unit is similar to the one described under 60.
71. French Patent 65,647/1,081,179—10.2.1954—F. Ecal
In order to counteract the oxidation of the developing solution, a partition is arranged close to the surface of the liquid
72. French Patent 1,093,313—17.2.1954—Soc. Construction d'App. de Photocopie
Apparatus according to 3. A motor can be coupled thereto.
73. Dutch Patent 89,247—5.3.1954—F. W. Ruys
Instead of guide walls, a carrier is provided which grips the leading edge of the sheets and carries them to the pressure rollers where they are released.
See also Part 5—Chapter 1—reference 15.

74. German Utility Model 1,683,979—3.4.1954—Wolf G.m.b.H.
A flat exposure unit and a developing tank which is operated by a motor-drive mechanism are arranged in one complete set.
75. German Patent 1,045,801—3.4.1954—Wolf G.m.b.H.
A copying apparatus comprising a guide member, a lamp and two transparent rollers is built above the developing section. One of these rollers is made of a transparent material thus enabling the light emitted by the lamp to penetrate this roller and expose the negative.
76. German Patent 935,529—3.4.1954—Wolf G.m.b.H.
Exposure device for diffusion transfer reversal process. Microswitches control the automatic switching on and switching off of the lamp and the transport system.
77. French Patent 1,133,377—27.4.1954—Wolf G.m.b.H.
Combination of the apparatus according to 75, 76 and a simple copying unit for the exposure of books.
78. United Kingdom Patent 755,881—30.4.1954—Kennedy Instruments Ltd.
The negative and the positive material are attached separately to a drum having a peripherical surface which is greater than the length of the materials. At least one sheet is moistened, preferably by a wick and this moistening step occurs shortly before the locus where both drums contact each other.
79. French Patent 66,618/1,081,179—5.5.1954—F. Ecal
The motor is arrested after a definite period. This period is adjusted as a function of the length of the materials.
80. French Patent 1,105,003—21.5.1954—Schwienbacher
Pressure rollers and tank unit are arranged separately. The tank unit is in fact a set of 3 compartments mounted one above the other. The central compartment contains no liquid: dry positive material.
81. United States Patent 3,048,486—21.7.1954—Peerless Photoproducts
1.2.1960
An apparatus is described which comprises short vertical separating members, guide members installed through the whole of the tank and pressure rollers arranged above the liquid.
82. German Patent 1,086,125—24.8.1954—Lumoprint-Zindler K.G.
The negative and the positive material each follow a separate path, only one of them being moistened.
The guide members are of equal length and are shaped to curve in opposite characteristics.
83. German Utility Model 1,686,762—30.8.1954—Lumoprint-Zindler K.G.
Guide members of a plastic material are covered in front with stainless steel. The pressure rollers are propelled towards each other by means of springs.
84. German Patent 959,615—6.9.1954—W. Uhrig
Instead of sliding the sheets into separate slots, the positive and the negative sheet cover each other and are carried together between two rollers. Each roller is provided with one suction cup to which the sheets remain adhering. Somewhat further on the sheets are stripped off the roller and each sheet is guided to a slot and then transported through the developing solution.
85. German Patent 1,025,718—8.9.1954—Dr. Böger K.G.
The outside inlet guide members are spring-biased so that their extremities in the developing solution presses against each other. These extremities may be provided with free rotating rollers.
86. German Utility Model 1,689,146—11.9.1954—Ad.Gerlach
Vertically tensioned wires provided with small beaded parts serve as guide members to move the negative and the positive material into the developing solution. An endless belt transports both materials through the liquid and out of the apparatus. Rollers which rotate in contact with the endless belt press the negative and positive materials together.
87. French Patent 75,551/1,081,179—27.10.1954—F. Ecal
Undulated guide members which do not run parallel to each other are of a special shape designed to make the least possible contact with the materials. Behind the inlet guide members a transport belt carries the materials to the pressure rollers.
88. French Patent 75.552/1,081,179—13.12.1954—F. Ecal
Semi-automatic device for driving the motor and the rollers; it allows a second sandwich of sheets to be treated before the first one has left the device.
89. Belgian Patent 544 284—14.1.1955—Gevaert Photo-Producten N.V.
The negative material is immersed before it is pressed on the positive which is moistened on one side only.
90. French Patent 1,140,562—26.1.1955—G. Schwienbacher—K. Pfister.
Diffusion transfer reversal process characterized by the fact that the solvent for the non-used silver halide is contained in the positive material. The apparatus used is an Eisbein apparatus (3) which has only one slot.

91. Swiss Patent 329,760—26.1.1955—Wiss.Forschungsinstitut—Zürich
Transferred to Lumoprint-Zindler K.G.
After the exposure, the original is transported out of the apparatus. The negative material controls a switch which causes the positive to move. Both materials meet each other in the developing solution and then travel together to the pressure rollers.
92. German Patent 1,014,434—16.4.1955—W. Eisbein
In order to counteract the buckling of the guide members, screws are provided which exert an adjusting tractive force on the guide members.
93. German Patent 1,020,866—27.5.1955—E. Leitz G.m.b.H.
The negative and the positive material are introduced into the apparatus from the two side walls. The guide members and the rollers bring the materials together between pressure rollers. The whole set-up is a stationary unit. When the apparatus is in use the tank containing the developing solution can be raised and when the apparatus is not in use the tank can be lowered. When the apparatus is not in use the developing solution is covered by a foil to prevent the developing solution from being oxidized.
94. German Patent 1,096,201—27.5.1955—E. Leitz G.m.b.H.
Similar arrangement as in 93—only the possibility of separating the negative from the positive material is novel. This step of separating the two materials is performed by an extra pair of rollers situated behind the pressure rollers.
95. United States Patent 2,946,272—22.7.1955—American Photocopy Equipment Comp.
A cylindrical exposure device of adjustable intensity is combined with a developing section in one unit. The developing section comprises a member for guiding the negative and the positive material separately from each other into the liquid, and also an undulated bottom part and guide members as well as a pair of pressure rollers mounted above the liquid.
96. German Patent 1,048,481—8.8.1955—Wolf G.m.b.H.
To prevent the oxidation of the bath, the developing liquid is flowed into a compressible bottle when the apparatus is not in use.
97. Swiss Patent 326,984—31.12.1955—D. Francey
Developing apparatus according to 3 characterized in that the pressure rollers are drawn by a delaying mechanism, so that a higher degree of regularity is obtained.
98. French Patent 1,143,397—15.3.1956—J. Ricord
A developing tank is placed on a plate which exerts pressure on a flexible bag containing the developing liquid. A flexible tube which is provided with a valve connects the bag to the tank. When the valve is opened and the tank is lowered the developing liquid flows through the tube into the tank. The level in this tank indicates the requisite height of the liquid. When this level is reached the valve is closed.
99. United Kingdom Patent 800,266—8.6.1956—Eastman Kodak
A pair of pressure rollers between which wires or a scraper run in order to prevent the sheets from rotating together with the rollers. No diffusion transfer.
100. Belgian Patent 551,474—3.10.1956—Gevaert Photo-Producten N.V.
Developing apparatus for use in daylight for X-ray material. The irradiated negative material is developed by immersion and pressed against the positive film. A positive image is formed by the diffusion transfer reversal process.
101. German Patent 1,085,425—19.10.1956—O. Slickers
The positive and negative materials are introduced into the apparatus, each from a side wall in it. Endless belts provided with suction cups grip the sheets, guide them through the developing solution and bring them together. Instead of pressure rollers, pressure plates are provided.
102. German Patent 1,111,941—7.1.1957—Lumoprint-Zindler K.G.
Exposure and developing unit in one apparatus. The exposure unit is kept very low since use is made of a spiral tungsten filament in a channel filled with an inert gas. The developing is done in an apparatus with a motor under the exposure unit.
103. United Kingdom Patent 851,384—27.2.1957—Van der Grinten N.V.
Apparatus for processing OCE-transfer material. This apparatus may also be appropriate for diffusion transfer. Two distinct embodiments. In the first one an endless belt carries both materials through the liquid; in the second embodiment a combination comprising an endless belt, transport rollers and lickrollers for moistening is used.
104. German Patent 1,083,426—27.2.1957—O. Slickers
A sponge-like tissue which sucks up the developer solution is fitted to the bottom of the apparatus. This tissue is protected by a perforated plate. When in use, the guide members and the transport rollers are pushed downwards so that the developing liquid is squeezed out of the sponge-like tissue and comes up out of the holes in the plate and moistens the materials.
105. German Patent 1,130,700—27.2.1957—O. Slickers
Two endless belts transport the negative and the positive material, respectively, through the developing liquid and make both materials meet to form a sandwich. Two possibilities are

provided, viz. either the transport belts are resilient enough to exert sufficient pressure to press the negative and the positive material together, or else further pressure is exerted by means of an additional set of two endless belts.

106. German Utility Model 1,745.522—16.3.1957—Bogiphot—Apparatebau
A flat exposure device in an upper position and a developing device in a lower position are combined in one apparatus. The negative and the positive material are introduced into the apparatus from the front. The sandwich of the two materials which have been pressed together also emerges from the front.

107. Italian Patent 578,919—9.9.1957—F. Gay
Exposure and developing units in one apparatus. The exposure is done in the upper section and the developing in the lower section. For this purpose, the developing tank is removed from the apparatus.

108. Belgian Patent 560,862—17.9.1957—Gevaert Photo-Producten N.V.
Rollers coated with silicon rubber prevent the sheets from rotating together with the rollers.

109. German Utility Model 1,757,449—9.10.1957—Lumoprint-Zindler K.G.
The apparatus in question contains an auxiliary means for transferring the negative image in the right position on to the aluminium plate. The auxiliary means consists of a stationary abutment member for the aluminium plate and an adjustable abutment member for the negative.

110. German Patent 1,052.812—28.10.1957—Wolf G.m.b.H.
Exposure unit and developing unit are combined in one apparatus. Whereas the exposure unit is located at the back, the front is occupied by a developing chamber with a partition in the centre. Two distinct types of material can be treated. One part of the apparatus is suitable for diazo treatment and the other for the diffusion transfer reversal process.

111. German Patent 1,146,365—7.11.1957—Lumoprint-Zindler K.G.
Automatic apparatus in which the exposure is done on a glass plate. The original is retained while the negative and positive are gripped by rollers after exposure and are conveyed through the developing section. A bottle containing a supply of developing liquid is also provided.

112. German Patent 1,103,762—27.11.1957—Lumoprint-Zindler K.G.
The negative and the original are introduced together into the apparatus and are gripped by an endless belt which passes these materials in front of an exposure unit. By means of a vacuum, the original is removed from the apparatus while the negative is conveyed through the developing tank where it contacts the positive material which follows a separate path.

113. German Patent 1,158,369—27.11.1957—Lumoprint-Zindler-K.G.
A curved guide member located behind the pressure rollers guides the sandwich back to the front of the apparatus in passing along the upper side of the latter. Here use is made of the heat emitted by the light source for drying the sheets.

114. German Patent 1,058,842—4.12.1957—Lumoprint-Zindler K.G.
Apparatus which is similar to 112. The original and the negative however, are not separated by vacuum but by brushes which produce static electricity by friction and thus attract the original and the negative.

115. German Patent 1,174,614—20.12.1957—Lumoprint-Zindler K.G.
Apparatus similar to 112. Here the original and the negative do not however have to be separated. A slot in the transport belt holds the original and carries it out of the apparatus after the exposure, whereas the negative is conveyed to the developing unit.

116. German Patent 1,099,352—23.12.1957—Optika
After the exposure, the sandwich formed by the negative, the original and the positive are gripped by two rollers which make the negative and the positive, each situated at the exterior, follow different paths. The original, being positioned in the middle, follows its normal course and is carried out of the apparatus. The negative and the positive are conveyed to the developing unit.

117. United Kingdom Patent 869,209—27.12.1957—American Photocopy Equipment Co.
The sandwich of negative and original and the positive are introduced at the same time into the apparatus. While the negative and the original pass in front of the lamp, the positive follows another path. After the exposure system, a separator or kicker member is provided. The original, preceding by a few mm the negative, pushes this kicker member upwards and reaches a path along which the original is carried to the outside of the apparatus. At the same time, the negative is conveyed to the developing tank whereas the positive which was blocked by the separator member is released and is also transported to the tank.

118. United States Patent 2,989,914—6.1.1958—K. R. Reick
A simple tank made of synthetic material is provided with reinforcing ribs.

119. German Patent 1,075,945—20.1.1958—Agfa A.G.
The step of mechanically separating the negative from the positive is facilitated if the sandwich of these materials is first heated intensely and then heated to a lesser degree. Two embodiments are provided: one with a rotating drum and the other with a heating channel.

120. German Patent 1,122,372—22.1.1958—Lumoprint-Zindler K.G.
The negative and the positive each follow a separate path along the lateral sides of the apparatus, after which the two sheets approach each other. The sheets are only moistened on one side since guide wires which prevent immersion are tensioned over the liquid surface. The height of the wires and the level of the liquid (birds fountain system) are critical. The moistened materials are transported out of the apparatus by means of pressure rollers.

121. United States Patent 3,001,463—23.1.1958—K. R. Reick
The developing system is similar to the one in 118. As an additional unit a continuously operating exposure device is provided.

122. United States Patent 2,925,025—28.1.1958—Copease Corp.
Three guide members are provided for transporting the negative, the original and the positive respectively. The first two guide members pass within close range of each other beneath the exposure lamps. The original is returned and leaves the apparatus. The negative and the positive come together in the developing section.

123. German Utility Model 1,794,536—1.2.1958—Agfa A.G.
For providing better separation of the negative and positive materials, the sandwiched materials are passed between heated rollers.

124. German Utility Model 1,793,573—1.2.1958—Agfa A.G.
This apparatus is intended for the same purpose as the one in 123 but the embodiment is slightly different in this case, the sandwiched materials pass over a heated plate.

125. German Patent 1,084,132—5.2.1958—Lumoprint-Zindler K.G.
Embodiment arranged vertically.
Two pairs of rollers, one pair of which is located in the tank containing the developing liquid and the other above the tank. When the rollers of both pairs are apart from each other, the negative and the positive can be introduced into the tank; when however the rollers are in the closed position the materials are transported upwards and are pressed together.
See also Part 7—Chapter 1—reference 16.

126. United Kingdom Patent 858,323—8.2.1958—Dr. Böger K.G.
Apparatus which can be fixed to the wall. When the negative and the positive are introduced into the apparatus, both materials are moistened by a spraying device. Over a curved bottom part, the negative and the positive material are guided to the pressure rollers. In the lower part of the tank a pressure roller which presses the materials against the bottom part is located. A continuously operating exposure device and circulating system for the developer are also provided.

127. German Patent 1,091,864—20.3.1958—Agfa A.G.
The negative and the positive adhering together are subjected, in the same plane, to pressure exerted from different directions by means of moving and stationary rollers. The positive is thus separated from the negative and dried.

128. United States Patent 2,986,987—22.3.1958—Lumoprint-Zindler K.G.
Complicated apparatus which comprises:
a first transport belt for transporting the original and the negative in front of the exposure unit; thereupon the original is carried outside the apparatus whereas the negative is moved in the opposite direction;
a second transport belt which carries the positive along;
guide wires which prevent the immersion of the negative and the positive;
a heating element for drying the sandwiched materials;
a birds fountain system which maintains the liquid at a constant level.

129. German Patent 1,126,248—5.4.1958—Lumoprint-Zindler K.G.
Exposure device.
The transport belt conveys the original and the negative in front of the lamps. The negative runs through a small slot formed by a pressure plate and a rotating roller, to the processing unit to which the positive is also moved. The original cannot be passed together with the negative through the narrow slot and is conveyed out of the device by the roller.

130. German Patent 1,128,748—5.4.1958—Lumoprint-Zindler K.G.
After the exposure, the original is conveyed out of the apparatus whereas the negative is conveyed to the developing device. As it travels, the negative comes into contact with a lever whereby the positive is also conveyed to the tank. Both materials are then gripped by pressure rollers.

131. German Patent, 1,085,036—24.4.1958—W. Eisbein
The original and the negative are passed between transparent rollers which transmit the light emitted by the lamps. A rotating drum and a whole series of transport rollers undertake the conveyance of the original out of the apparatus and the negative and the positive together arrive in the developing tank.

132. German Patent 1,121,474—28.4.1958—Lumoprint-Zindler K.G.
The sandwiched materials pass over a heated drum for the purpose of drying. The two materials are separated by making them travel over a strongly curved guide member and by conveying them thereafter between two rollers rotating in opposite directions.

133. German Patent 1,118,607—28.4.1958—Lumoprint-Zindler K.G.
Floating guide members.
The negative is immersed whereas the positive is only moistened superficially.

134. German Utility Model 1,884,167—30.4.1958—Lumoprint-Zindler K.G.
Fully automatic apparatus. A stack of negatives is situated on the bottom of the apparatus. A stack of positives is located at the top of the apparatus. When an original is put into the apparatus, a dry positive is obtained a short time thereafter. A set of cams, rollers and endless belts provide for the smooth operation of the apparatus. The used negative is stored in a special partition.

135. United States Patent, 3,043,413—11.6.1958—American Photocopy Equipment Co.
This apparatus is an improvement of the apparatus according to 117.
The mechanism for introducing the negative, the original and the positive is simplified. Only three rollers are provided instead of four rollers.

136. Swiss Patent 368,709—1.7.1958—F. Gay
A series of four curved tanks fit into each other and constitute in this way the channels and the guide members for the materials.

137. United States Patent 3,044,386—23.7.1958—Lumoprint-Zindler K.G.
Stacked negatives are located at the front of the apparatus.
Each time an original is introduced into the apparatus, a negative is gripped and is exposed together with the original. The original is removed from the apparatus. The positive at the top of the apparatus is released in due course so that the negative and the positive are conveyed together to the developing tank.

138. German Patent 1,125,769—16.8.1958—Lumoprint-Zindler K.G.
Fully automatic apparatus. The negative and the positive are each provided in roll form. While the negative is rolled up again after the diffusion transfer step, the positive is dried and cut off.
Both materials are moistened on one side only. A stamping device and a birds fountain system are provided. The fully automatic operation of the apparatus is secured by a magnetic track.

139. German Patent 1,130,701—16.8.1958—Lumoprint-Zindler K.G.
Obliquely stacked negatives located on the bottom of the apparatus are gripped one by one each time an original is introduced into the apparatus and are each conveyed to the exposure device. The positives at the top of the apparatus are released in due course so that both materials arrive together in the developing tank.
See also the apparatus under 137.

140. German Patent 1,091,432—28.8.1958—Agfa A.G.
The negative with cut off corners is stuck by adhesive tape to the front of the aluminium plate. The apparatus itself has small projections on the lateral sides which serve as guide members.

141. German Utility Model 1,779,293—10.10.1958—Lumoprint-Zindler K.G.
In order to reduce oxidation of the developing liquid a spare container with developing solution is positioned under the tank. When the apparatus is in use, developing liquid is circulated upwards towards the tank. When the apparatus is switched off a return member makes the developing liquid flow back into the spare container.

142. French Patent 1,204,169—10.10.1958—J. Maillard
Apparatus for the diffusion transfer reversal process, which comprises a flat exposure unit, an exposure timer and a spare container. The latter can be displaced upwards and is used for filling or emptying the tank.

143. German Patent 1,106,177—4.12.1958—Lumoprint-Zindler K.G.
Device for continuous exposure and a spare container which can be displaced upwards. The spare container is a flexible bag of a synthetic material. The level of the developing solution can be easily read.

144. German Utility Model 1,785,042—16.12.1958—W. Eisbein
A structure consisting of wires which accelerates the drying of the positives.

145. United Kingdom Patent 861,541—18.12.1958—W. Eisbein
In order to obtain a good exposure, very fine synthetic threads (1/10 mm) are tensioned between a light transmitting disk and a foamed rubber roller. These threads separate the original from the negative.

146. United States Patent 3,025,778—12.1.1959—American Photocopy Equipment Co.
Auxiliary means for exposing small documents. It consists of a support covered with a sheet of Mylar material. The document is placed between these two elements; the whole set is then introduced into an exposure device.

147. German Utility Model 1,828,604—2.2.1959—Dr. Böger K.G.
At the respective lateral sides, guide plates and roller pairs convey the negative and aluminium into the apparatus. Guide members which can be moved upwards and which are situated in the liquid, make both materials meet in the centre where they are pressed on to each other by pressure rollers.

148. Swiss Patent 366,189—11.2.1959—A. Hediger
Special shape of the tank. Tank and the guide members can be removed from the apparatus. Instead of the guide members, a second tank can be mounted in the apparatus. This provides a means of carrying out both the developing as well as the fixing processes.

149. United States Patent 2,996,969—17.2.1959—A. Kaufman
A cylindrical rotating lamp, auxiliary rollers and guide members provide for the transport of the materials through the exposure unit.

150. German Utility Model 1,865.364—24.2.1959—Lumoprint-Zindler K.G.
The negative material is located in a drawer above the apparatus whereas the positive material is situated on the bottom of the apparatus. The original and the negative travel together in front of the lamp; while the original is carried out of the apparatus, the negative is carried to the developing tank. As it travels, the negative pushes a lever whereby the positive is also made to travel. The positive and the negative are carried together to the developing liquid. A supply container is connected to the tank. It is possible to connect a pump.

151. German Utility Model 1,822 804—24.2.1959—W. Eisbein
In order to hold the negative and the aluminium sheet in register, both sheets are carried together along a lateral abutment member to synthetic wires; these wires separate the negative and the aluminium sheet again from each other and carry them to the transport rollers which convey the separated materials in register with each other to the developing tank.

152. German Patent 1,114,387—6.3.1959—W. Seidel
Apparatus with concave guide members, one of them being located at the top and the other at the bottom. The non-moistened positive material travels at the top while on the bottom the negative material controls a microswitch which actuates a spraying device, which causes the negative material to be sprayed with developing solution. At the end of the path, both the negative and the positive material meet between two pressure rollers. A second microswitch switches off the spray of developing liquid and switches the device over to a water spraying action for a short time during which the apparatus is cleaned.

153. German Patent 1,098,815—12.3.1959—Bogiphot Apparatebau
Combination of a flat exposure device and a developing tank. Between the developing tank and the supply tank a pump is provided which is coupled to a motor capable of rotating in two directions. A floating switch and a reheating device may also be provided.

154. German Patent 1,096,202—18.3.1959—W. Eisbein
The negative and the original pass in front of an exposure device. Transparent wires positioned between the two materials make the original and the negative material each follow a different path.

155. German Utility Model 1,792,493—18.3.1959—W. Eisbein
A portable cabinet provided with: a battery and a transformer, an exposure unit, a developing device, cassettes for the negative and the positive material and bottles containing developing liquid.

156. United States Patent 3,057,282—6.4.1959—Eastman Kodak Co.
Special apparatus.
A number of rollers axially rotating close to each other constitute a cylinder filled with processing liquid. An embodiment is designed and disclosed for the diffusion transfer reversal process. The negative and the positive material arrive between different rollers in the cylinder containing the liquid and are pressed together by other rollers which convey the materials out of the apparatus.

157. United Kingdom Patent 873,719—13.4.1959—American Photocopy Equipment Co.
Sheet separator device.
Special embodiments of the separator or kicker member of the apparatus already mentioned under 117.

158. Swiss Patent 367,707—16.4.1959—A. Hediger
Cylindrical supply bottle which adjusts the level of the liquid.

159. United States Patent 3,024,716—25.4.1959—Lumoprint-Zindler K.G.
Automatic apparatus in which the materials forming the sandwich are not separated. After the exposure, a stripper is provided which carries the original out of the apparatus and conveys the negative to the developing tank. The positive is transported automatically and arrives together with a negative in the tank containing developing liquid. The supply bottle is built in.

160. United States Patent 3,031,941—26.4.1959—W. Eisbein
The negative and the original which are separated by thin wires, pass together in front of the lamp. The original is carried to the outside of the apparatus. The negative reaches a slot where it controls a microswitch. As a consequence thereof a definite length of material is cut off from the roll containing the positive material and is advanced. The negative and the positive meet in the tank.

161. German Patent 1,128,294—13.5.1959—Lumoprint-Zindler K.G.
After the negative has been exposed to the original in a position at a distance from the latter, the original is transported to the outside of the apparatus, while the negative is gripped by a swinging element which carries it along to the developing tank. The positive located on the bottom is also transported to the developing tank by the transport rollers at the right moment. The negative and the positive, separated from each other, are passed through the liquid whereupon they are gripped by pressure rollers.

162. German Patent 1,148,140—14.5.1959—Lumoprint-Zindler K.G.
After the exposure step the negative travels alone and during its travel it actuates a lever which provides for the release of a positive and travels together with the negative through the developing tank. The transport system for the positive is novel and consists of an endless belt provided with ribs. In each rib a positive is located in an upright position. As the belt turns downwards the positive is received between two guide members which guide the positive to the developing tank.

163. German Patent 1,130,292—14.5.1959—Lumoprint-Zindler K.G.
This patent relates to a more specific embodiment of the arrangement according to 162. The patent only relates to the separation of the original from the negative by means of a rotating roller.

164. German Patent 1,174 162—29.5.1959—Lumoprint-Zindler K.G.
A rotating resilient arm pushes at each rotation one original from a stack of obliquely positioned originals and feeds it between a transport roller and an endless belt. In this way the original and a negative material in roll form join each other between a light source and a pressure roller. The original leaves the apparatus whereas the negative joins the positive material which is also in roll form. Both materials travel with a space between them to the developing tank. Immediately before entering the latter both materials are cut off.

165. German Patent 1,096,200—29.5.1959—Dr. Böger K.G.
One of the inlet guide members is provided with a resilient extended part which effects a rubbing action on the material whereby the air bubbles are removed.
Particularly intended for aluminium offset materials.

166. Italian Patent 610,169—3.6.1959—F. Gay
Relates to an exposure and developing apparatus for the diffusion transfer reversal process and other processes. The developing section is composed of tanks of different sizes and positioned one above the other.

167. United States Patent 3,040,692—12.6.1959—Robertson Photo-Mechanix Inc.
Reproduction camera with built-in developing device for negative and aluminium. After exposure, synchronously rotating transport rollers provide for the step of transporting the negative and the aluminium sheet together in the tank. Here both materials are gripped by a rotating swing element and are carried to the pressure rollers.

168. German Patent 1,187,135—6.7.1959—Lumoprint-Zindler K.G.
Flat exposure device provided with superposed developing tank of the conventional type. The pressure system of the exposure unit is formed by springs intended for adapting the material surface to be exposed to each thickness of the original (sheet or book)

169. German Patent 1,157,481—15.7.1959—Lumoprint-Zindler K.G.
The negative and the positive material are located on one support. After the exposure both materials pass through a developing tank. Guide members are not necessary here. Thereupon the negative is peeled off.

170. United States Patent 3,097,585—17.7.1959—Speed-O-Print.
A flexible bag of a synthetic material containing the developing liquid is attached to the lid at the rear of the device. Filling and emptying of the developing tank is done by opening and closing the lid.

171. German Patent 1,102,558—29.7.1959—W. Eisbein
In order to maintain the negative and the aluminium support in register with each other during the developing step a few levers are mounted at the inlet of the apparatus. At the front of these levers, rollers are mounted, and at the rear blocking elements are located. When the rollers are opened, the blocking elements close the entrance and the negative and the aluminium support are placed between the guide members to reach as far as the blocking elements. When the rollers are shifted in relation to each other the blocking elements are displaced and both materials travel to the pressure rollers. These rollers rotate synchronously with the first rollers.

172. United States Patent 3,017,816—13.8.1959—American Photocopy Equipment Co.
The original and the negative pass together in front of the cylindrical exposure device. The original leaves the apparatus; the negative material reaches a switch. A positive in an obliquely upright position is thereby released and slides together with the negative through the developing liquid to the pressure rollers.
The special shape of the lid of the tank prevents the oxidation of the developing liquid.

173. German Utility Model 1,799,592—14.8.1959—W. Eisbein
A flat plate attached to the lower guide members and reaching as far as the point of contact of the two pressure rollers helps to keep the negative and the aluminium offset plate in register.
174. German Utility Model 1,799,589—20.8.1959—Lumoprint-Zindler K.G.
A spare tank and a pump are mounted under the diffusion transfer apparatus. The oxidation of the developing liquid in the spare tank is prevented by means of a floating lid (made of rubber or synthetic material).
175. United Kingdom Patent 947,717—9.9.1959—Lumoprint-Zindler K.G.
A rotating cylinder provided with a carrier member make the negative and the original travel in front of a light source. While the negative is freed and advances to the developing tank the original is further transported and is carried to the outside along the front wall of the apparatus. The positive travels synchronously with the negative so that both materials arrive together in the developing tank and travel to the pressure rollers. The developing liquid is maintained at a constant level by means of a supply container provided with a birds fountain system. Means are provided for marking the negative during exposure.
176. German Patent 1,146,754—11.9.1959—Lumoprint-Zindler K.G.
Same apparatus as described under 175.
The United Kingdom Patent 947,717 claims the priority of German Patent Application L. 34,167 German Patent 1,146,754 is issued from the German Patent Application L 43,127.
177. German Utility Model 1,800,095—15.9.1959—Lumoprint-Zindler K.G.
Flat exposure device with an obliquely positioned lateral wall for making it easier to copy pages from books. A developing device is provided on front of the exposure section.
178. German Patent 1,112,893—27.10.1959—Wolf G.m.b.H.
A flexible bag of synthetic material on the bottom of the apparatus is connected to the developing tank. When the tank is pushed downwards, the developing liquid flows into the tank. In the inoperative position the tank is placed in a higher position whereby the developing liquid flows back into the flexible bag.
179. German Patent 1,124,814—13.11.1959—Lumoprint-Zindler K.G.
The exposure and processing part is similar to the one mentioned under 161. When a sheet of negative material is pulled out of the drawer containing the negative material a sheet of positive material is automatically placed on the right path. Later on the negative and positive materials come together in the developing tank.
180. German Utility Model 1,805,966—25.11.1959—Lumoprint-Zindler K.G.
An auxiliary means for maintaining the aluminium offset plate and the negative material in register with each other during the processing stage. This means comprises not only guide members but also gripping members which hold the materials until they are gripped by the pressure rollers.
181. United States Patent 2,989,913—24.12.1959—Nord Photocopy and Electronics Corp.
A flexible bag of synthetic material is located under the tank and is compressed by a lever driven by a motor so that the developing liquid flows into the tank. In the inoperative position the liquid flows back into the bag.
182. United States Patent 3,031,942—4.1.1960—Speed-O-Print
This apparatus is a combination of:
a cylindrical lamp with a rotating endless belt,
a tank with guide members and pressure rollers and a closed light-tight path for the sandwich of negative and positive material,
a motor driving the endless band and the pressure roller,
a flexible bag of synthetic material containing the developing composition and attached to the rear wall,
dispensers for the negative and the positive material.
183. German Patent 1,148,139—28.1.1960—Lumoprint-Zindler K.G.
The construction of this apparatus is different from that of the conventional immersion type apparatus. The negative and the positive material, separated from each other, are introduced into the apparatus. Between the two materials there is a spraying chamber which is connected with a reservoir. A rod at the entrance of the apparatus is pushed away by the paper, thereby freeing an opening in the reservoir and thus allowing the developing liquid to flow to the spraying chamber in which the negative and the positive are moistened.
After the passage of the materials the rod returns to its original position and closes the reservoir.
184. German Patent 1,150,282—1.2.1960—Photorapid A.G.
This apparatus comprises guide members which can be lifted out of the apparatus for the purpose of maintaining the negative material in register on an aluminium offset plate. At first the front edges of the aluminium plate and the negative are made to adhere together. There are two possible embodiments:

(1) a roller which can be swung into the upright position and which is situated between the negative and the aluminium plate,
(2) a curved guide member which can be lifted out of the apparatus, and which can be arranged between the aluminium plate and the negative material and which again can be returned to its original position in the apparatus.

185. United States Patent 3,203,335—29.2.1960—A. B. Dick Co.
A reprocamera according to 167.
The claims relate only to the details of the swinging system which carry the negative and the aluminium offset plate through the tank containing the developing liquid. A replenishing system to maintain the developing liquid at a constant level is also provided.

186. United Kingdom Patent 882,957—1.3.1960—A. Corona
Spraying system—no step of immersing.
The bottom of the apparatus is a reservoir for the developing liquid. A pump makes the developing liquid pass through small perforated tubes and moistens in this way the negative and the positive material. When both materials are pressed on each other the excess of liquid is flowed back to the bottom part.

187. United Kingdom Patent 981,886—17.3.1960—Gevaert Photo-Producten N.V.
To bring the negative material into register on the aluminium offset plate, the aluminium plate is first placed between the pressure rollers. The negative is pushed between the guide members through the developing liquid towards the inoperative pressure rollers. Before these rollers the negative contacts a microswitch which actuates the pressure rollers and presses the negative and the aluminium plate together.

188. German Patent 1,207,795—17.3.1960—Lumoprint-Zindler K.G.
Relates to an apparatus and a process for the treatment of material containing developing substances which give up bound water. One example is given in which application for the diffusion transfer reversal process is disclosed.
The negative and the positive material, separated from each other, are introduced into the apparatus. Both materials have been moistened on the front surface by a roller containing the above mentioned chemical substances while the back is heated. Both materials are then transported to the pressure rollers where they are pressed together.

189. Austrian Patent 3653/60—17.3.1960—Photorapid A.G.
Auxiliary means of maintaining the negative material in register with the aluminium offset plate. A line mask contributes to the exact positioning of the original and the negative during the exposure.
On an assembly plate with lateral edges the negative is made to adhere firmly to the aluminium plate.

190. German Patent 1,178,708—29.3.1960—Dr. Böger K.G.
Spraying system.
Between straight guide members a spray nozzle is positioned through which nozzle the developing liquid is pumped for moistening the negative and the positive material. The excess of developing liquid is flowed back to the spare container.

191. Belgian Patent 590,300—1.4.1960—Gevaert Photo-Producten N.V.
Wires are positioned to prevent the sheets from adhering to the rollers.

192. Japanese Patent Application 5496/63—7.4.1960—T. Daimon
The negative and the positive material, *separated from each other*, are introduced between two inlet rollers into the apparatus. A curved bottom part and a centrally rotating drum guide the materials to the pressure rollers. A first small guide member keeps the materials separated from each other and a second guide member transports the negative and the positive material to the pressure rollers.

193. United States Patent 3,095,796—18.4.1960—A. B. Dick Co.
Connected to the developing tank is a supply container which fills the developing tank when the latter has taken up its highest position. When the supply container is lowered the developing liquid flows from the tank into the supply container. In this latter position the pressure rollers also move away from each other so that adhering by crystallization is prevented.

194. German Patent 1,132,435—23.4.1960—W. Eisbein
A simple automatic apparatus.
The original and the negative material, separated from each other by fine wires, pass together in front of a lamp. While the original is transported out of the apparatus, the negative together with the positive material reach the developing tank. A special driving and coupling mechanism is provided to make the negative and the positive material move at an equal speed.

195. German Patent 1,170,783—23.4.1960—W. Eisbein
Automatic apparatus.
The positive material in roll form is pushed against a continuously rotating roller by means of a flexible plate actuated by a switch which is controlled by the negative, and in this way the positive is transported to the developing tank. During its travel it is cut and joins the negative.

196. Swiss Patent 376,769—24.4.1960—Photorapid A.G.
Apparatus without guide members.
Two embodiments:
(1) The negative and the positive material are respectively transported into the apparatus through two slits. The curved bottom part guides the materials beneath the roller to the pressure rollers.
(2) There is only one opening—in the form of a slot—which has concave or convex walls and which is shorter than the width of the negative and the positive. The special shape of the slot ensures that both the materials, separated from each other, reach the liquid.

197. German Patent 1,173,803—28.4.1960—Lumoprint-Zindler K.G.
Combination of an apparatus for continuous exposure and a developing device. A novel feature which should be mentioned is that the exposure device is not only provided with a conventional gas discharge lamp but also with a U.V. and an I.R. light source.

198. German Utility Model 1,855,625—7.6.1960—Lumoprint-Zindler K.G.
Combination of an exposure device and a developing apparatus. To facilitate cleaning the bottom part of the developing tank and for replenishing the latter, the exposure device which is attached by a hinge is tilted out of the way. The arrangement is such that even with a device for continuous exposure only one driving mechanism for the steps of exposing and developing is necessary.

199. United States Patent 3,101,036—8.6.1960—Speed-O-Print
Disposable cartridge for use in photocopy machine. A flexible bag packed in cardboard having one opening for removing the connecting piece which is connected to the developing tank.

200. German Patent 1,125,768—9.6.1960—W. Eisbein
Thin resilient guide members instead of the conventional elements made of hard material. In order to prevent the last part of the material from deforming the guide members, a built-in rod which slackens the upward movement is provided.

201. German Utility Model 1,821,144—23.7.1960—Lumoprint-Zindler K.G.
An auxiliary means for treating materials of small sizes. The arrangement comprises two flexible PVC-sheets, each fitted to a lateral part of the arrangement, and provided with grippers in which the negative and the positive material respectively, can be placed. At the moment when the materials are gripped by the pressure rollers, the auxiliary means is withdrawn from the apparatus.

202. German Patent 1,191,229—20.7.1960—Chen Wen Kuo
A spray nozzle which is placed between the horizontal guide member which is protected in the upward direction, so that only the material passing underneath it (which is the negative) is moistened. The positive which passes above it remains in a dry state. Either a circulating pump system may be provided or a supply container may be located above the apparatus from which the developing liquid flows freely to the spray nozzle. A reservoir is located underneath for collecting the used developing liquid.

203. Swiss Patent 384,369—11.8.1960—Photorapid A.G.
A combination of a flat exposure device and a developing apparatus. A drying chamber is built in under the exposure device. The heat originating from the lamp is blown into this chamber.

204. German Patent 1,135,761—22.8.1960—Dr. Böger K.G.
When materials of large sizes are pressed together creases may occur in them. These can be avoided by using a combination of a small pressure roller with a much larger roller which has been polished. As a result, the sandwich of the negative and the positive material is wound round the larger roller without showing any creases. Thereupon the larger roller is swung away from the small roller and the sandwich of both materials can be unwound and separated.

205. United Kingdom Patent 929,869—7.9.1960—E. Wender
The negative and the positive material, separated from each other, are introduced between two inlet rollers and directed between the guide members to reach the liquid. A spare container is located above the guide members. Different embodiments of continuous exposures are described. The used up developing liquid can be collected. The developing tank is provided with grooves for the purpose of collecting the deposits. Any droplets flowing back from the pressure rollers are likewise collected.

206. German Utility Model 1,821,146—8.9.1960—Develop G.m.b.H.
For the purpose of detecting the end of a roll of negative or positive material these ends are perforated in some areas to permit a microswitch to actuate a detecting system.

207. German Patent 1,187,481—26.9.1960—Lumoprint-Zindler K. G.
In order to avoid mistakes in the step of pressing the developing liquid out of a flexible supply bag and of flowing it into the developing tank, a spring-loaded element which adjusts the pressure exerted is provided. The essential feature of this patent is that the spring is pulled out until a definite point is reached where it is brought to a position of rest.

208. Japanese Patent Application 13,749/63—5.10.6160—Oriental Photo Industrial Co.
Rather cumbrous embodiment having the sole advantage that the two materials need not be pushed into the apparatus. For carrying out this step, the lid of the apparatus is provided with sub-divisions which form a kind of rack. When the lid is opened, the negative and the positive, separated from each other, can be placed in the racks. When the lid is closed, the negative and the positive material arrive in the developing liquid where they are gripped by the pressure rollers.

209. United States Patent 3,113,499—24.10.1960—Speed-O-Print
Apparatus for diffusion transfer process with continuous exposure unit. During the exposure the original and the negative are rotated on a cylindrical glass roller around the lamp. A removable ejector plate provides therefore that the materials leave the glass roller.

210. German Patent 1,184,214—18.11.1960—Lumoprint-Zindler K.G.
Automatic apparatus in which the negative and positive materials are each contained on a roll. While introducing the original between two endless belts, a microswitch is switched on. This microswitch controls the driving of the negative and the positive materials and also, in due course, the serving of these materials. The negative together with the original pass in front of the exposure device. The original is reconveyed out of the apparatus while the negative meets the positive in the developing tank. A supply container for the developing liquid is built in to the tank.

211. United States Patent 3,110,241—7.12.1960—G.A.F. Corp.
Relates to a fully automatic apparatus comprising the step of separating the negative from the positive, which form a sandwich. The original and the negative in roll form, pass in front of the exposure lamps and then return to a receiving tray. The positive, also in roll form, is cut off somewhat before reaching the developing tank, and arrives in the developing tank together with the negative. The sandwich, i.e. the cut off positive and the negative, being still in roll form, now travels in an upward direction and the negative then changes direction at a sharp angle and is wound up on a core. This bending off movement, frees the positive and it leaves the apparatus.

212. United States Patent 3,148,611—20.12.1960—American Photocopy Equipment Co.
The original and the negative are exposed by a rotating fluorescent tube. The spare container with a barometric feeding arrangement is placed above the developing liquid. The separating element which maintains the negative and the positive in separate positions is widened under the liquid level so that the materials are prevented from adhering together.

213. United Kingdom Patent 993,565—21.12.1960—A. Corona
The purpose of this patent is to make the positive follow a shorter path than the negative material in the developing liquid. This is done either by straight guide members or by inlet rollers combined with an endless belt. Both materials pass right above the bottom part under an idler rotating guide roller. The curved shape of the developing tank makes the materials travel to the pressure rollers. The developing liquid stored in a synthetic bag is located above the developing tank. The bag is smashed so that the liquid is flowed into the tank.

214. German Utility Model 1,830,696—24.12.1960—Develop G.m.b.H.
The developing liquid contained in a synthetic container is located in a frame which is attached by a hinge to the developing tank and is connected thereto by means of a flexible tube. When the container is turned upwards, the liquid flows into the tank. In the lower position, the developing liquid returns to the container. Under the developing tank a dispenser is provided for supplying the negative and the positive materials.

215. Japanese Patent Application 20,694/63—26.12.1960—Olympus Kogaku Co.
Relates to a device for moistening the negative and the positive material with a definite quantity of liquid, immediately before pressing the materials to each other. On one side, a rotary pump is connected with channels leading to the materials and on the other side it is connected with the developing tank (container).

216. United States Patent 3,000,630—29.12.1960—R. Slate
Paper separating mechanism. Two inlet rollers guide the negative and the positive material to the developing tank. The separating element makes the materials enter the tank separately, one material preceding the other, by a few millimeters and both materials meet each other only at the pressure roller station. The device consists of a first separator rod of elliptical shape placed at an angle of about 45° to the plane of feed of the negative and positive, and a pair of post-separation guide rods.

217. German Patent 1,144,113—27.1.1961—Dr. Böger K.G.
The offset sheet and the negative material are introduced separately into the apparatus and are conveyed along a curved guide member to the pressure rollers. Somewhat above this curved guide member, a guide roller with a hollow central part is arranged so that only the edges of the materials contact this roller.

18. French Patent 1,316,396—6.3.1961—Lumoprint-Zindler K.G.
Apparatus for treating diffusion transfer reversal material containing substance which give up bound water. The negative and the positive material are submitted to a linear pressing treatment in which the temperature is increased preferably to 90–120°C.

219. German Utility Model, 1,835,290—10.4.1961—Dr. Böger K.G.
Auxiliary means for pressing the developing liquid packed in a flexible bag into a developing tank situated in a higher position. The bag is located on a plate which is kept in an upright position by means of two flexible springs. Above the bag which is connected to the tank, a lid is located. When the latter is pressed in downwards, the developing liquid is squeezed into the tank and the springs are also compressed. These springs serve as a brake to prevent the sudden spraying of the developing liquid into the tank. Once the bag has been pushed low enough, the lid is blocked. When the lid is released, the liquid flows into the flexible bag.

220. French Patent 1,294,806—17.4.1961—J. Maillard
The flexible bag containing the developing liquid is placed under the developing tank. The bag is connected to the tank by means of a flexible tube. A firm plate situated above the liquid bag is connected with a lever fitted to the outside of the apparatus. There are two possibilities: either the liquid is pressed into the tank or additional springs cause the pressure plate to be lifted up again and the developing liquid to flow into the flexible bag.

221. United States Patent 3,218,918—28.4.1961—Microcard Reader Corporation
Machine for enlarging a microphotograph and for making a photocopy of the enlarged image of the microphotograph. Negative and positive are both contained in roll form. The exposed negative and the positive, separated from each other, are transported by means of a pair of transport rollers to and through the developing tank and they are pressed between pressure rollers, to form a sandwich. Right in front of the entrance of the developing tank, the negative and the positive materials are severed.

222. German Utility Model 1,839,335—2.6.1961—Ravenna Bürotechnik.
Apparatus which is built according to the stack assembly system. The motor, the tank and the guide members are removable. The three straight guide members have the same form.

223. United States Patent 3,112,685—12.6.1961—J. Fluke and R. Bennett
Apparatus with circulating pump and spray system which provides for a good equal moistening of the materials. Inlet supports for the negative and the positive (aluminium offset-plate) are located at either side of the apparatus. Both materials are gripped at the same time by the inlet rollers, guided towards each other and pressed on to each other. First the negative is moistened by spraying with developer liquid while the lower travelling positive material is then also moistened by the effluent developer liquid. The exact matching of negative and positive material (maintaining in register) is done visually and manually.

224. German Patent 1,200,685—7.8.1961—Photorapid A.G.
Automatically operating apparatus wherein the original and the negative material are together submitted to exposure; the original is retransported out of the apparatus and the negative and positive arrive together in the developing tank where they are pressed together. In order to be able to separate the original from the negative after exposure, a small thin metal tab is placed on the front of the original. A solenoid ensures that the original follows a different path from that of the negative after the exposure.

225. Belgian Patent 607,041—9.8.1961—Gevaert Photo-Producten N.V.
Apparatus for preparing copies by the silver complex diffusion transfer reversal process, comprising a pair of opening inlet rollers, a set of cams, a developing tank with guide members and pressure rollers. When the inlet rollers are moved away from each other, the cams close the entrance and the negative and the aluminium plate can be brought into register with each other. When both rollers are closed, then the materials can be moved towards the pressure rollers. When the materials enter the developing tank, they are pressed against the respective guide plates by means of the idler rotating rollers.

226. German Patent 1,890,499—11.9.1961—Agfa A.G.
The negative is moistened on one side whereas the positive is not moistened at all. A flat developing unit, in which a container maintains the liquid at the same level, comprises guide members so that in fact the negative slides with its emulsion side over the surface of the liquid. Right in front of the pressure rollers, the negative meets the positive which is stacked under the developing tank. The positive material can also be held in roll form. A means is also provided whereby the developing liquid can be flowed back from the tank into the container.

227. German Utility Model 1,883,285—11.9.1961—Agfa A.G.
This apparatus is similar to the one described under 226. The guide members of the apparatus according to 226 for only moistening the emulsion are here replaced by a non-absorbing lick-roller with a very matt surface which carries along the liquid and in this way moistens the emulsion.

228. German Patent 1,176,015—12.10.1961—Photo-Entwicklungsgeräte A.G.
This patent relates to an apparatus in which the developing liquid is added drop by drop by exertion of a slight pressure on a more or less flexible container.

229. United Kingdom Patent 1,014,497—14.10.1961—Wolf G.m.b.H.
The developing tank with guide members is provided with a special discharge member, so that all of the developing liquid can flow away into a flexible bag when the apparatus is not in use.

230. French Patent 1,305,022—2.11.1961—A. Durand
A simple and practical way for arranging the pressure rollers in the walls of the apparatus.

231. United States Patent 3,182,578—7.12.1961—Lumoprint-Zindler K.G.
Automatic apparatus in which the introduction of an original makes the negative and the positive material move in such a way that the original and the negative are exposed together. The negative material runs synchronously with the positive so that both materials arrive at the same moment in the developing tank where they are pressed together. A separating element provides for the retransportation of the original to the outside of the apparatus.

232. United Kingdom Patent 1,037,051—23.1.1962—Block & Anderson
A separator member is placed between the front sides of both materials adhering together. When the whole set is introduced between the guide members of the developing tank, then the separator member remains blocked at the inlet between the guide members and provides therefore that the aluminium and the negative are sufficiently spaced from each other to make the developing liquid enter between both materials.

233. United States Patent 3,202,074—29.1.1962—Speed-O-Print
The air chamber under the guide members of the developing tank allows the adjustment of the level of the developing liquid by means of one and the same quantity of liquid. By opening a valve a large or a small quantity of air can escape and so the level of developing liquid can be lowered.

234. United States Patent 3,121,381—5.2.1962—Copease Corp.
Combined exposure device and developing apparatus. The novelty resides here in the variation of the light intensity during the exposure step. The original and the negative material travel over a transparent plate made of synthetic material under which the lamp is positioned. The distance from the lamp to this plate is a measure of the light intensity. The displacement of the lamp is done by a turn switch located at the front side of the apparatus.

235. German Patent 1,204,940—14.2.1962—Lumoprint-Zindler K.G.
Circulating pumping system.
The pump and the motor are located in the developing liquid right above the bottom part of the spare container. The whole set can easily be removed. The developer liquid provides also for the cooling of the motor. The operation of the apparatus is noiseless.

236. German Patent 1,250,265—17.2.1962—Lumoprint-Zindler K.G.
Same execution as the apparatus mentioned under 183. Here however the developing liquid is heated. Heating elements are located in the spray chamber.

237. Japanese Publ. Patent Application 6648/64—13.3.1962—Ricoh
Complicated developing apparatus.
On introducing a negative material the actuation of a microswitch provides therefore that a positive material starts moving at the other side of the apparatus. Both materials travel together along curved guide members to the central part of the apparatus where they are pressed on to each other after they have been moistened. Uniformity in moistening is obtained by a double moistening procedure. The first moistening is done by means of a lick roller; the second moistening is done immediately before the materials meet each other. In the central part of the apparatus is situated a chamber into which developing liquid is pumped. The liquid is flowed at the upper side around the already mentioned curved guide members to a collecting tank located at both sides of the apparatus and in this collecting tank the already mentioned lick roller rotates. By means of an overflow in both tanks the developing liquid is carried to a reservoir from which the operation cycle is restarted.

238. German Utility Model 1,890,500—16.3.1962—Lumoprint Zindler K.G.
The negative and the aluminium offset plate are maintained in register during the developing step. At the start, there are only guide members on the lateral walls, but farther on there are guide members over the full width. The mutual distance between the guide members thus decreases gradually.
The aluminium and negative materials are fixed by their rear sides and are not released until the materials are situated between the rollers.

239. United States Patent 3,145,635—31.3.1962—Lumoprint-Zindler K.G.
The apparatus comprises a continuous exposure device, a flexible bag containing developer liquid, and a developing tank provided with a lid, located in the upper part of the apparatus. When the lid is opened, the bag with the developing liquid is squeezed and the developing liquid flows into the tank. On closing the lid, the developing liquid flows back into the bag.

240. United States Patent 3,078,777—2.4.1962—Speed-O-Print
Relates to a very simple developing tank and guide members. The guide members are placed at a well-defined angle.

241. United Kingdom Patent 976,786—3.4.1962—Lumoprint Zindler K.G.
The developing tank contains 3 superposed parts. On the bottom part there is a flexible bag containing developer liquid which bag is connected by a pipe-line to a pump which in its turn is connected to a higher located developing tank. A floater system in the developing tank actuates via a microswitch system the pump which makes the developer liquid circulate in upward direction. When the liquid in the tank reaches the desired level, the pump is then arrested via the floater system and the microswitch.

242. German Utility Model 1,885,789—18.4.1962—Develop G.m.b.H.
The developing tank is connected with a flexible bag situated underneath it. A rigid plate on the flexible bag is pressed downwards by means of a lever under the influence of a spring so that the developer liquid flows into the developing tank. When the push-button is released the developer liquid flows back into the bag.

243. German Utility Model 1,854,284—19.4.1962—Develop G.m.b.H.
A pump operating in only one direction is connected with a two-way valve which enables the liquid to be pumped to and from the developing tank.

244. German Utility Model 1,854,286—19.4.1962—Develop G.m.b.H.
Automatic apparatus wherein the original and the negative, separated from each other, are passed in front of an exposure device and wherein after the exposure the original is carried out of the apparatus and the negative together with a synchronously travelling positive material arrive in the developing tank.

245. German Patent 1,172,537—27.4.1962—Lumoprint-Zindler K.G.
The developing tank is provided with a collecting reservoir located underneath it and a pump. The overflow system which determines the quantity of developing liquid is connected in an air-tight manner with the collecting reservoir. As soon as the desired liquid level is attained by the pumping operation, a closed circulating cycle is formed thereby. On arresting the pump the tank containing the developing liquid is emptied into the collecting reservoir.

246. Belgian Patent 617,582—14.5.1962—Gevaert Photo-Producten N.V.
To maintain the negative and an aluminium offset plate in register with each other during the processing step, blocking elements are provided between the pressure rollers and the guide members. The resistance of these blocking elements can only be overcome by the abutment of the aluminium sheet. The blocking elements can be constituted by non-driven pressure rollers or by cams. Both sheets have to be introduced into the apparatus in such a way that the negative is the first to reach the blocking elements.

247. Japanese Patent Publication 9595/64—22.5.1962—Fuji Fotofilm
Relates to a non-conventional apparatus.
After the opening of the pressure rollers, the negative material is introduced into an obliquely located tank in the apparatus. After a definite time a driving system in this tank provides therefore that the developed negative is retransported in an upward direction to contact a positive material which has been previously moistened by a lick roller. Along the now closed pressure rollers a sandwich of both the materials pressed together leaves the apparatus.

248. German Utility Model 1,876,358—23.5.1962—B. Nielsen
Relates to various embodiments for transporting one of the materials in a dry state and for carrying the other material moistened on one side only through the apparatus, and for pressing them on to each other.

249. Japanese Publ. Patent Application 9596/64—24.5.1962—Fuji Fotofilm
One of the two materials travels through the liquid; the other material is moistened on one side only by means of a lick roller. The squeezed out developing liquid is removed along a small channel situated under the pressure rollers.

250. Belgian Patent 618,238—29.5.1962—Gevaert Photo-Producten N.V.
Apparatus for maintaining the negative material and the aluminium offset plate in register with each other; it comprises a flat support, inlet rollers, guide members and pressure rollers.
The novelty resides here in the inlet pair of rollers. The lower roller is considerably thicker than the upper one. This latter roller can however move over a path which is concentric with the peripheral surface of the lower roller. The materials remain pressed together but on displacement of the upper roller the negative and the aluminium plate arrive between different guide members which carry them to the developing liquid.

251. United States Patent 3,121,436—11.6.1962—A. Bernstein
Guide members guide the negative and the positive material, separated from each other, to the developing tank. An endless belt and two pressure rollers transport these materials and press them together.
In the developing tank itself only little liquid is present but a reservoir situated above the developing tank allows the latter to be easily replenished with fresh developing liquid.

252. United States Patent 3,165,998—1.6.1962—K. Reick
Photocopy machine with developer solution storage and supply means including a developing solution tray, an expansible and contractable solution container, mounted at a lower elevation than the said tray, a pivotally mounted pressure plate and a crank arm manually operable to actuate said pressure plate.

253. United States Patent 3,216,341—14.6.1962—Pacer International Corp.
Conventional apparatus.
Very narrow claim. The novelty lies in the fact that the lid of the apparatus serves as a guide member.

254. German Utility Model 1,896,369—20.6.1962—Lumoprint-Zindler K.G.
Relates to an automatic apparatus.
The original, the negative and the positive material are transported together into the apparatus. Whereas the movement of the positive is temporarily arrested, the original and the negative pass in front of the exposure device. The original is carried to the outside of the apparatus and the negative follows a path which leads to the developing tank. During its movement the negative actuates a switch which restarts the movement of the positive material in such a way that the negative and the positive arrive in the developing tank at the same moment.

255. United States Patent 3,315,582—28.6.1962—American Photocopy Equipment Inc.
On introducing the negative and positive materials a short separating member situated above the level of the liquid separates both materials by pushing them from each other so that the developer liquid can reach these materials without being hindered.
A round bottom part serves as a guide member for transporting the negative and positive materials to the pressure elements. These latter elements consist of a combined arrangement of a roller and an endless belt.

256. German Utility Model 1,858,240—11.7.1962—Develop G.m.b.H.
Pertains to a special arrangement comprising:
storing station for the negative and positive materials,
storing station for the chemical substances,
drier in which heated air is blown on to the finished positive,
device for destroying the negative.
Above the arrangement an apparatus for carrying out the diffusion transfer reversal process can be placed.

257. United States Patent 3,179,031—8.8.1962—R. Gordon
The processing part is a conventional apparatus but the exposure device is novel. The negative and the original are placed in an envelope (a carrier member) consisting of two rigid plates of synthetic material the upper plate of which consists of a transparent material. This carrier member is slid under the apparatus where it is gripped by a driving roller which provides for the further transport of the carrier member. Above the path followed by this envelope a lamp of adjustable intensity is located.

258. United States Patent 3,198,104—14.8.1962—Anken Chemical Film Corp.
A portable photocopying apparatus.
Besides the exposure device the apparatus contains furthermore a developing tank, a reservoir section and a storage bag. These latter three elements are connected with each other. When copying is finished the machine is closed and placed in an upright position; after about 2 minutes (to allow the developing liquid to flow from the tray into the cartridge) a button on the outside is pressed to seal the developer in the cartridge. For use, the apparatus is placed horizontally on a table.

259. Dutch Patent 120,590—22.8.1962—Machinefabrick Buhrs en Zonen
The negative and positive materials are introduced into the apparatus from two different sides. Two rollers rotating at the same speed carry the materials along, transport them to the developer and thereupon press them together. The rollers are provided with grippers for gripping the negative and the positive material and for releasing them at the right moment. Solenoids provide for the switching on and switching off the apparatus.

260. German Patent 1,171.269—25.9.1962—Lumoprint-Zindler K.G.
Heating elements are provided for treating materials containing products which give up water.

261. German Utility Model 1,902,352—13.10.1962—Lumoprint-Zindler K.G.
Automatic apparatus in which the negative and the positive material are contained in roll form and which is also provided with a pump system for the developer. The original actuates switches which control the transport and the severing of the negative and the positive. After exposure the original is carried to the outside of the apparatus while the negative and the positive arrive together in the developing tank.

262. German Patent 1,225,489—15.11.1962—Lumoprint Zindler K.G.
Guide members which are situated right at the level of the liquid provide therefore that one of the materials is moistened on one side only. The level is adjusted by a birds fountain system.

Under the curved bottom part and parallel thereto a second guide member is located so that the second material is transported in a dry state to the pressure rollers.

263. Belgian Patent 640,241—23.11.1962—A. B. Dick (Holland) N.V.
Two large rollers not only transport materials through the apparatus but also press the moistened materials together. The step of moistening is done by lick rollers which may rotate in opposite directions.

264. French Patent 1,347,914—24.11.1962—J. Maillard
One of both materials runs along the upper part of the apparatus and is moistened on one side only by means of a large lick roller. The second material runs over the curved bottom part, passes under this roller and travels through the developer to the pressure rollers.

265. United Kingdom Patent 996.527—14.12.1962—A. Fisken
This patent relates only to the members (guide vanes) which separate the negative and the positive material on their introduction into the apparatus. The lower part thereof forms an angle so that both materials arrive in the developer at a farther distance from each other. The surface of the said guide vanes are provided with dimples.

266. German Utility Model 1,871,483—7.1.1963—B. Nielsen
A flexible bag containing the developing liquid is connected with the developing tank by means of a special connecting piece. The level of the liquid can be adjusted by modifying the position of the lever which is used for pressing the bag.

267. United States Patent 3,208,323—14.1.1963—Microcard Reader Corp.
Pertains to a re-aligner for paper roll photocopying machines. Applies to a detail of the apparatus mentioned under 221. Negative and positive are made to travel in register with each other.

268. French Patent 1,353,559—15.1.1963—R. Beiké and P. Séguret
Relates to a pumping system to permit the introduction of the liquid into the developing tank, and to maintain the liquid at a given level and to remove it.
The use thereof in the diffusion transfer reversal process is not described.

269. German Utility Model 1,870,294—2.2.1963—B. Preikschat
Pertain to an auxiliary means of preventing the sandwich of the material from rotating together with the rollers and of allowing the operator to have both hands free for further handling. This means consists of a stand having on its upper side a small roller over which a string can be passed. One end of the string is provided with a gripping element and the other end with a counterweight. When the sandwich leaves the pressure rollers the string is fixed thereto by means of the gripper. The counterweight pulls both materials in an upward direction.

270. Dutch Patent Application 288,817—11.2.1963—Gevaert Photo-Producten N.V.
The negative material is fixed on to a rotating cylinder. This cylinder carries the negative material over a lick roller and a scrape roller. It comes into contact with the positive and is pressed thereto. The cylinder guides both materials as far as a separating station, where a knife separates the positive from the negative material.

271. French Patent 1,357,692—25.2.1963—M. Hemery.
A part of one of the guide members is extended as far as the level of the developing liquid. The lateral walls of this guide member form a kind of tank with this arrangement whereby one of the materials can be passed to the pressure rollers in a dry state.

272. French Patent 83,196—addition to 1,347,914—6.3.1963—J. Maillard
See also arrangement according to 264.
Under the curved bottom part mentioned in the arrangement according to 264 a second parallel wall is provided so that one of the materials is made to travel to the pressure rollers in a dry state.

273. United Kingdom Patent 1,034,563—1.4.1963—Lumoprint-Zindler K.G.
The negative material is moistened superficially and the positive is kept dry.
Combination of:
a flexible reserve tank supported between a fixed plate and a plate movably mounted upon a spring means
a sealed supply container
bath arranged to contain a developer liquid having a meniscus at a predetermined level
the diameter of a first connecting pipe is related to the diameter of the outlet and to the diameter of a second connecting pipe so that the reserve tank is emptied on compression thereof when the meniscus in the bath is at the predetermined level.

274. German Utility Model 1,875,004—19.4.1963—Dr. Böger K.G.
Use is made of an auxiliary means for maintaining the original, the negative material and the aluminium offset plate in register during the steps of exposing and developing. This auxiliary means consists of a metal base plate provided with abutment members on to which the aluminium offset plate, the original and the negative materials are placed. On top of this a magnetic pressure plate is provided for pressing the materials on to each other. When the materials are correctly

positioned the negative and the aluminium offset plate are then stuck together by means of a strip of tape.

275. United States Patent 3,295,430—27.4.1963—Lumoprint-Zindler K.G.
Flat exposure device with slanting walls which allow prints to be easily made from books. A special pressing system presses the books firmly against the exposure plate. The developing tank is built in.

276. German Patent 1,256,297—27.4.1963—Lumoprint-Zindler K.G.
Adjustment of the exposure time.
One of the pressure or transport rollers is provided with a hollowed extension in the form of a spiral. Resting in this spiral a pointer which is shifted by the turning of the spiral and which interrupts the exposure. The exposure is a function of the displacement of the pointer, being longer for a small displacement and shorter for a large displacement at the beginning of the exposure.

277. United States Patent 3,236,168—22.5.1963—American Photocopy Equipment Company
Relates to a combined container, tray and paper guides for a photocopying machine. The container itself comprises the guide members for guiding the materials to the pressure rollers. The apparatus is provided at its front only with some separating elements as already described in the arrangements according to 212 and 255 and is provided at its back with the usual pressure rollers. One needs only to cut off the two upper parts of the container and to place them in the apparatus.

278. German Utility Model 1,926,598—28.8.1963—F. Arnold
The negative and the positive material are introduced into the apparatus at the upper side thereof. Both materials are only moistened on one side by means of a rotating porous roller which is connected to a supply container. Two endless belts guide the materials to a set of pressure rollers. The sandwich of both the materials leaves the apparatus at its lower side.

279. United States Patent 3,171,341—4.9.1963—R. Gordon
The exposure parts have already been described in the arrangement according to 257.
The developing apparatus does not comprise separating elements. Only two slots are provided through which the negative and the positive material are introduced into the apparatus. Between the free rotating roller and a curved bottom part both materials travel to the pressure rollers.

280. German Patent 1,204,521—9.9.1963—Robertson Photomechanix Inc.
See also the arrangement according to 167.
The upper sheet of a stack of negatives is removed by means of a vacuum and is carried to the exposure device and thereafter to the developing tank.

281. German Utility Model 1,962,372—18.9.1963—Wolf G.m.b.H.
Relates to an automatic operation for adjusting the level of the liquid in the developing tank by means of two electrodes. A lever actuated by a motor presses the developing liquid out of the flexible bag into the developing tank. When the liquid reaches the two electrodes the current to the motor is cut off. When the level of the liquid decreases then the liquid is again pressed out of the flexible bag until the liquid again reaches the electrodes.

282. Belgian Patent 653,438—23.9.1963—Gevaert Photo-Producten N.V.
Apparatus for separating sheets, the leading edge of the one material preceding somewhat the leading edge of the other material. The leading edge of the first material actuates a microswitch so that it is gripped by two rollers which advance the material in question and at the same moment a pressing rod exerts a rubbing contact on the trailing material and deflects this material at a sharp angle so that it is forced to separate from the other material.

283. German Patent 1,212,840—25.9.1963—Agfa A.G.
The negative material contains substances which under the influence of heat give up bound water. As mechanical heating has many disadvantages use is made here of heating by means of a liquid (e.g. silicon oil). The negative material is moistened on its back surface by this heating liquid and is thereafter pressed on to the positive. The moistening is done either by means of a lick roller or by an operation whereby the negative material is slid with its back surface over guide members lying at the same height with respect to the liquid level.

284. German Patent 1,238,773—4.10.1963—Ravenna Bürotechnik
The positive material travels in a dry state beneath the tank and is carried to the pressure rollers. The negative material is moistened by a lick roller. The guide members and the lick roller are however constructed in such a way that the leading part of the negative is not moistened. Both materials are pressed together by means of two pressure rollers. Behind these pressure rollers are located two separating rollers which, due to the fact that the front part is not adhering, are capable of separating the negative from the positive material.

285. French Patent 1,379,093—11.10.1963—M. Hemery
For maintaining the negative material and the aluminium plate in register with each other during the transport of these materials in the developing tank, a centering table is placed in

front of the developing part and on this centering table both materials are correctly positioned. In the front of this arrangement there is a pair of inlet rollers which, in the open position, allows both materials, in register with each other, to pass through the separating station straight into the tank. When these inlet rollers are closed, the materials pass through the developing liquid in such a way that the negative material is moistened by means of lick rollers whereas the aluminium sheet passes through the liquid. Before the materials have passed the inlet rollers, the negative material and the aluminium sheet are gripped and pressed together by the pressure rollers.

286. United Kingdom Patent 1,074,476—11.10.1963—M. Hemery
This arrangement is an extension of the arrangement according to 285.
It contains in addition:
a lick roller and special guide members
a flexible bag located under the developing tank

287. German Patent 1,211,489—30.10.1963—Lumoprint-Zindler K.G.
Relates to an apparatus for the separation of sheets wherein the leading edge of one material somewhat precedes the leading edge of the other material. The said leading edge is directed between two rollers by means of a swing lever. The rollers and the lever are connected with each other in such a way that when the negative material is gripped by the rollers the lever is displaced and clears the way for the positive material which is not similarly diverted but travels straight forward. For drying the positive a heating element is built in.

288. Belgian Patent 655,054—2.11.1963—A. B. Dick N.V.
The arrangement relates to an air-tight, closed pivotable supply container which maintains the liquid in the developing tank at a constant level (bird fountain system). When the arrangement is not in use the supply container is turned downwards so that the liquid can flow back from the developing tank into the supply container. By displacing the guide members one of the materials can be kept in a dry state.

289. French Patent 1,416,091—19.11.1963—Wiss. Forschungsinstitut
The original together with a negative travel in front of an exposure device. While the negative is transported to the developing tank, the original on its way to the outside actuates a lever whereby the positive material is released and meets the negative after it has been moistened by a lick roller. The developing tank contains only a small quantity of liquid which, prior to use, can be pressed out of a more or less flexible supply container, which is located on top of the apparatus. The liquid can also be supplied automatically when the introduced negative actuates a switch which is connected with a mechanism for pressing on the supply container.
See also Part 7—Chapter 1—reference 17.

290. Dutch Patent 300,921—22.11.1963—Machinefabriek Buhrs en Zonen
On either side of the apparatus obliquely positioned abutment tables are provided on which tables the negative material and the aluminium offset sheet respectively are located. Each of these tables leads to a set of inlet rollers. At least one of these pairs of inlet rollers can be disconnected from the motor and can be rotated by hand for positioning the positive and negative materials directly opposite to each other. Separate developing tanks are provided for each material.

291. United States Patent 3,261,277—27.11.1963—Lumoprint-Zindler K.G.
Vertically arranged apparatus in which the upper part constitutes the separating elements and the pressure rollers and wherein the lower part constitutes the developing tank. In this tank are also located the guide members and a pair of transport rollers. Along two separate guide members the negative and the positive material are guided to the developing tank where they are gripped by the transport rollers and are transported through the developing liquid. After some time these rollers rotate in the reverse direction and make the materials leave the developing liquid again in an upward direction, guide them between the pressure rollers and carry them farther to the outside of the apparatus.

292. French Patent 1,416,752—3.12.1963—Agfa A.G.
Relates to a developing apparatus for materials containing developing substances and substances which give up bound water. The temperature of the heated surfaces is from 80°C to 220°C. Two transport rollers the upper one of which is heated, transport the negative, running with its back in contact with the heated roller, over the guide members to the pressure rollers. The positive is also transported to the pressure rollers the upper one of which is also heated, and the positive is conveyed over the bottom part of the apparatus by means of two transport rollers and guide members.

293. French Patent 1,419,101—5.12.1963—Agfa A.G.
Apparatus similar to the one disclosed under 292.
The heated upper transport roller and the pressure rollers are replaced by heated curved pressure plates.

294. Japanese Patent Publ. 869/66—17.12.1963—Olympus Optical Co.
Portable apparatus. A closed storage tank is connected to the developing tank by means of a

section plate, which has a hole at the bottom. When the apparatus is placed vertically the developer then flows into the storage tank. When the apparatus is placed horizontally the developing liquid then flows into the developing tank. An exposure device can be included.

295. United States Patent 3,332,435—14.1.1964—American Photocopy Equipment Co.
A pumping arrangement for a photocopying machine.
Besides automatic replenishment, means is provided for flowing the developing liquid from the developing tank back into the supply container.

296. Belgian Patent 652,767—20.1.1964—Speed-O-Print
The guide members for the negative material pass through the developer whereas the positive material is passed above the liquid level and is maintained in a dry state. Both materials meet each other immediately in front of the pressure rollers.

297. Belgian Patent 652,768—24.1.1964—Speed-O-Print
The guide members for the positive which is not moistened, are located under the developing tank where the negative material passes through. The developing tank is connected on both sides with a supply container for the developer.

298. United States Patent 3,277, 808—29.1.1964—B. Cahan
The step of guiding and registering the negative and aluminium offset plate occurs during the processing. The guide members, the inlet and the pressure rollers are mounted in a pivotable arrangement. Before introducing the material, this arrangement is moved to a locus above the liquid and the materials are introduced between their respective inlet rollers and guide members. When this arrangement is moved back into the developer and when the transport mechanism is switched on the negative and the aluminium sheet then remain in register during the processing.

299. French Patent 1,391,938—29.1.1964—M. Hemery.
The apparatus comprises a developing tank with guide members and pressure rollers, a pressing system for a flexible bag containing developer and a continuous exposure device. The latter device contains a rotating cylinder and a curved guide plate which is forced against the cylinder by means of springs.

300. United States Patent 3,247,959—16.3.1964—Anken Chemical & Film Corp.
Cartridge for processing solutions used in diffusion transfer photocopying machines comprising an inner bag to hold the developer, a collapsible jacket, an outer envelope and a tube connected to the inner bag. The liquid can be flowed from the cartridge by applying a difference in height or by exerting a pressure.

301. Dutch Patent Application 6403125—24.3.1964—A. B. Dick N.V.
Relates to a process for separating sheets adhering together wherein the leading edge of the one material is somewhat in advance of the leading edge of the other material. The leading edge of the first material is deflected and arrives between transport rollers which further transport the deflected sheet. The second sheet continues travelling along its original path.

302. French Patent 1,433,792—1.5.1964—Eastman Kodak Co.
Heated pressure rollers provided with a thermostat.

303. French Patent 85,738/1,347,914—13.5.1964—J. Maillard
A circulating pump system for the developer.

304. United States Patent 3,291,024—28.5.1964—American Photocopy Equipment Co.
Machine with a one-piece base construction which allows the various parts to be simply dropped into place so that the complete assembly and dismounting can be carried out quickly and efficiently. During exposure means are provided to prevent the endless belt from deviating from its normal course.

305. Belgian Patent 667,663—30.7.1964—Gevaert-Agfa N.V.
Process for separating the sandwich formed by the negative and the positive material The sheets adhering together pass between a pair of rollers and thereby actuate a microswitch which controls the mechanism for driving the rollers. The upper roller starts rotating in the opposite direction and the lower roller remains inoperative. As a consequence thereof the uppermost material is forced to curl and to form a loop until the leading edge of the sheet passes along the upper roller and is transported between the rollers of a second pair of rollers in another direction. The first pair of rollers starts rotating again in the original direction to continue the further movement of the lower sheet.

306. Belgian Patent 670.200—28.9.1964—Gevaert-Agfa N.V.
Immediately before the positive is pressed against the negative the back of the positive is moistened with processing liquid. Curling of the positive is thereby avoided. The negative is moistened by a lick roller.

307. French Patent 1,423,759—23.10.1964—Eastman Kodak Co.
Relates to a fully automatic apparatus with the negative material contained in roll form and the positive in sheet form. The circulating pump system for the developer is started when an original is introduced into the apparatus. Although only the use of a hardening developer is

described the apparatus could also be used for processing materials by the diffusion transfer reversal method of processing.

308. United Kingdom Patent 1,132,067—27.11.1964—Eastman Kodak Co.
Liquid handling device for regulating the supply of liquid from a collapsible container to a developing tray and a closed reservoir. The reservoir is mounted above the collapsible container and the tray and is provided with a birds fountain system for maintaining a constant level of the liquid in the tray.

309. Dutch Patent Application 6,414,510—14.12.1964—Machinefabriek Buhrs en Zonen
The negative and aluminium offset plate are maintained in register during the developing stage. Two guide plates with abutment members provide for the correct positioning of the offset plate and the negative material. Inlet rollers and separated guide members provide for the transport of the materials, whether moistened or not, through the apparatus.
Between the end of the guide members and the pressure rollers two transport rollers are arranged at such a distance from each other that they can only start moving the negative in combination with the aluminium plate. The aluminium plate is first introduced into the apparatus and remains between the transport rollers until it is joined by the negative material. They are pressed together by means of pressure rollers.

310. Dutch Patent Application 6,501,533—9.2.1965—G. Nix
Feed members provide for the freeing of the uppermost sheet of quantities of obliquely stacked negative and positive materials. While the negative and the original pass together in front of an exposure device, the positive material passes directly to the developing tank where the negative and the positive material are pressed on to each other.

311. Belgian Patent 661,443—22.3.1965—Gevaert-Agfa N.V.
Apparatus for separating the negative and the positive wherein the leading edge of one sheet precedes the leading edge of the other sheet. After moistening by a lick roller the negative contacts the positive and is pressed on to it. The sandwich of both the materials leaves the apparatus over pivotable guide members behind which a pair of rollers and a microswitch are arranged. The leading edge of the negative is gripped by the pair of rollers and the microswitch is actuated. A solenoid makes the pivotable guide member move into a downward position and the positive material is made to follow another path.

312. French Patent 1,437,584—24.3.1965—J. Maillard
The negative and the positive material are introduced separately into the apparatus, each at one lateral side thereof. After moistening by lick rollers the sheets are gripped by pressure rollers pressed against each other. Means are provided for making the two lick rollers and the lick rollers together with the pressure rollers, rotate against each other.

313. French Patent 1,437,585—24.3.1965—J. Maillard
A sufficient quantity of developer is sprayed between two pressure rollers for the development of one negative and one positive material. The spray nozzle is located immediately above the pressure rollers. A light beam and a photo-cell provide therefore that when the negative and the positive are introduced into the apparatus the spray system starts to operate.

314. United States Patent 3,354,807—18.6.1965—R. Hoe & Co.
An aluminium printing plate device is provided with a pair of pressure rollers which are partly immersed in the developer liquid contained in a tray and a guide member for guiding the plate and the negative material from either side of the apparatus in such a way that both materials arrive together into the nip of the rollers and are passed to each other while moving farther between the pressure rollers. The tank containing the developer liquid is provided with a shaft journalled in its lateral walls, the shaft carries blades which vigorously agitate the developer solution as the shaft is rotated.

315. German Utility Model 1,945,458—6.9.1965—H. Kohler
Circulating pump system for developer.
A device is provided with two straight guide members and an extended curved guide member. One of the pressure rollers rotates in the liquid.

316. Dutch Patent Application 6,616,492—25.11.1965—Lumoprint-Zindler K.G.
Developing apparatus for materials which contain no nuclei. Two superimposed tanks contain respectively a solution containing nuclei and a developer solution.
Both tanks are connected to a flexible container which can be emptied by exerting a pressure. While the negative passes through the developer solution the positive passes through the nuclei-containing solution. Before the negative and the positive material are pressed to each other, they are squeezed off.

317. French Patent 1,518,165—12.4.1966—Ball Office Equipment
The apparatus comprises a developing tank, a continuous exposure device, a flexible supply container and an air bag connected to an air pump. When the bag is filled with air then the developer is flowed from the supply container into the developing tank under the influence of pressure.

318. French Patent 1,489,071—25.4.1966—Eastman Kodak Co.
Before two materials are made to contact each other and are pressed to each other a determined quantity of liquid is sprayed between both materials.
319. French Patent 1,489,019—28.4.1966—Speed-O-Print
By raising or lowering a flexible bag the developing tank is filled or emptied.
320. French Patent 1,515,446—18.5.1966—Lumoprint-Zindler K.G.
See also arrangement according to 316.
A lick roller applies the nuclei-containing solution on to the positive material. Before the positive material is made to contact the negative material the excess of liquid is removed from the positive by means of scraper rollers.
321. German Utility Model 1,944,635—8.6.1966—Dr. Böger K.G.
A supply container for developer is built under the developing tank and a bag capable of being blown up is also provided. The supply container and the bag are connected with each other. There is also provided an air pump which is connected to the bag. When air is pumped into this bag then the developer is flowed from the supply container so that the developing tank is filled.
322. French Patent 1,489,481—15.6.1966—M. Hemery
See also the arrangement according to the French Patent 1,379,093, according to 285.
Applies to an improved apparatus.
It comprises specially constructed guide members and a flexible supply bag containing developer which bag can be pressed.
323. Dutch Patent Application 6609363—5.7.1966—M. Spoon
By raising or lowering a closed supply container the developing tank can be filled or emptied.
324. German Utility Model 1,951,393—9.9.1966—B. Nielsen
Preparation of offset plates according to the diffusion transfer reversal process.
The developing tank is constructed aside of the exposure device. The glass plate of this exposure device serves also for maintaining the negative and the aluminium offset plate in register with each other. The characterizing features of this arrangement lie in the narrow guide members and inlet rollers. A vacuum provides for good contact between the original and the negative during exposure.
325. German Utility Model 1,952,302—9.9.1966—B. Nielsen
See also arrangement according to 324.
The inlet rollers mentioned according to 324 and the driving system are carried out in such a way that the aluminium plate can be introduced between the rollers over a determined distance and maintained in place.
326. German Utility Model 1,958,026—9.9.1966—B. Nielsen
Auxiliary means for facilitating the registering of the original, the negative and the offset plate. The means consists of a transparent envelope provided with markings.
327. German Utility Model 1,958,411—31.10.1966—Wolf. G.m.b.H.
Device comprising a flexible dispenser which contains developer. The force of the lever is not used for compressing the dispenser but is only intended for tensioning a spring. In releasing the spring the bag is emptied.
328. United States Patent 3,360,258—25.11.1966—G. Nix
Photocopy paper package to be used in the apparatus as described for the arrangement according to 310.
329. BB 716,310—31.8.1967—Gevaert-Agfa N.V.
Only one sheet of material is used instead of the usual two sheets of material (positive and negative material). Exposing and developing a photographic light-sensitive material which comprises a non-transparent flexible support sheet, a light-sensitive silver halide emulsion layer, and a layer containing a white or coloured pigment and a hydrophilic colloid binder.
The light-sensitive material is held stationary in the apparatus while the original is scanned by a travelling carriage provided with mirrors and an objective and in this way the material is exposed. After exposure the material is cut off, transported to the developing tank, and developed.

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